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Aqueous tape casting process for hydroxyapatite

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Abstract

The condition for the preparation of stable hydroxyapaptite (HA) slurries by aqueous tape casting was identified. To acquire stable low-viscosity slurries, the influences of dispersant, binder and plasticizer on the rheological properties were investigated. The slurries of submicron sized HA behaved as near Newtonian up to a solid loading of 56.1 vol%. Films of HA had very good qualities, such as homogeneity, surface quality, and so on. Results indicated that slurries at selected conditions met the needs of tape casting process.

Keywords: Tape casting; Hydroxyapatite; Mechanical properties; Biomedical applications

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1. Introduction

Hydroxyapatite (HA) has potential applications as a bioceramic material due to its chemical and biological similarity to bone tissues and good biocompatibility, osteoconductivity, and bone-bonding properties.[1–6] HA has been shown to stimulate osteoconduction and is a material that can be integrated into bone without provoking an immune reaction. Generally, hydroxyapatite ceramic takes many different forms, such as powders,[7] granules,[8] pellets,[9] dense and porous ceramics,[10,11] and cements.[12] However, the brittleness and insufficient strength of hydroxyapatite limits its application to physiologically nonload-bearing bone lesions.

It is evidenced that laminated design is a feasible path to increase the strength and the fracture toughness.[13,14] Recently, many researchers show their interest in applying laminated object manufacturing (LOM) technology to build parts from engineering materials, such as structural ceramics and composites. LOM is one of the rapid prototyping and manufacturing techniques where a part is built sequentially from layers of paper, green sheets of ceramics, sheets of metal, etc. This technique is especially suitable for producing geometrically complex objects, and for operating with a high degree of automation.[15–19]

Tape casting is a convenient shaping method to produce two-dimensional thin ceramic plates of usually 10–1000 μm thickness.[20–22] A paste-like suspension consisting of powder, solvent, dispersant, polymer (binder) and plasticizer is cast onto a substrate by a moving blade in a constant distance to the substrate. The final dried green tape is flexible, not sensitive to mechanical stresses and thus, easy to handle. This processing method as well as the equipment are simple and therefore are interesting for many types of applications, such as dielectrics for capacitors, chip carrier substrates and sensor supports.

Tape casting has traditionally been performed using organic solvents as dispersing liquid media but there is now a trend to move away from organic solvents and an expected transition towards water-based systems.[23–25] The main advantages for switching from organic to a water-based system are reduced health and environmental hazards coupled with a lower cost. But, in comparison with organic solvent-based tape casting slurries, aqueous tape casting systems have a smaller tolerance to minor changes in processing parameters, such as composition, and drying conditions. Thus, it is of utmost importance to understand and control the rheology of water-based tape casting slurries. The viscosity of slurries must be low enough and the slurry should exhibit pseudoplatic behavior. Thixotropy and any other time dependent behavior are undesired, because in this case the rheological behavior would be dependent on the pretreatment of the suspension.

Compared with other technologies, aqueous tape casting has great advantages in producing homogeneous and flat tapes

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without causing environmental problems. Therefore, the use of aqueous-based slurries for tape casting becomes an increasing trend in the fabrication of ceramic substrates.

In this work, we studied the effects of the dispersant, pH on the dispersing ability of HA particles, the rheological behavior of the slurries and the tape casting performance, focusing on the quantity of polymer dispersant. The mechanical and microstructural properties of as sintered HA samples were also studied.

2. Experimental procedure

2.1. Synthesis of HA powder and characterization

The hydroxyapatite was prepared using a precipitation method. The appropriate amounts of 0.3 M H_3PO_4 (Sinopharm Chemical Reagent Co. Ltd.) solution was added into $Ca(OH)_2$ (Sinopharm Chemical Reagent Co. Ltd.) suspension using an automatic titrator with vigorous stirring. During the addition, the pH of the solution was maintained at 10.0 by the addition of NH_4OH solution. The reaction mixture was stirred for 2 h and aged for 1 day at 25 °C. The resulting precipitate was filtered, dried at 90 °C overnight. After drying, the HA powder was calcinated at 900 °C for 2 h in air to obtain submicron-sized HA particles.

The phase composition of the as-synthesized and the calcinated powder was determined by X-ray diffraction (X-ray diffractometer, Model RAX-10, Rigaku, Japan). The chemical compositions of the samples were determined by chemical analyses. A SICAS-4800 photo size analyzer was used to measure the size and distribution of the particles.

2.2. Zeta potential test

The aim of this study was to find the conditions for possible electrostatic stabilization in the suspension, and to observe the dispersant influence on the particle surface electric charge. Zeta Plus (Brookhaven Instruments Corp., U.S.A.) was used to measure the Zeta potential of HA powders at various pH values. HA suspensions (0.01 vol%) were prepared in the absence and presence of PAA-K (kalium polyacrylate) at various pH values, which were adjusted using HCl or NaOH for the acid or basic solutions, respectively.

2.3. Preparation of HA slurry

Aqueous HA slurry was prepared by, respectively, mixing HA powder as well as dispersant into distilled water. Slurries were ball milled with ZrO_2 balls for 48 h, followed by adding pre-prepared PVA solution as the binder and ethylene glycol as the plasticizer. The slurries were further ball milled for another 12 h.

2.4. Rheological analysis

The Rheological behavior of as-prepared HA suspensions with solids loading in the range 25–56.1 vol% were investigated using a coaxial flat rheometry (SR-5 Rheometric scientific instrument company, America). Apparent viscosity of the suspensions under different shear rate was tested under steady shear conditions by ascending and descending shear rate ramps, respectively.

2.5. Tape casting and sintering

After homogenizing, the slurries were degassed under vacuum to remove air bubbles. Finally, Tape casting was performed on Procast Precision Tape Casting Equipment (Division of the International, Inc., Ringoes, New Jersey) with the gap height of 250–600 μm. After drying freely in open air at room temperature for some time, green tapes were obtained.

It was heated up to 600 °C at a heating rate of 30 °C/h and held for 1 h to slowly burn out all organic additives. It was then heated up at 5 °C/min. Final sintering was carried out at 1300 °C and held for 1 h, for densification.

2.6. Microstructural analysis

Microstructure of the both the binder-removed film and the sintered body were observed using a scanning electron microscopy (SEM, JSM-6700F, Japan). The density and apparent porosity of the sintered samples were measured using Archimedean method.

2.7. Mechanical measurement of green tape and sintered ceramics

The tensile tests of green tapes were performed at a constant load speed of 2 mm/min at a span length of 30 mm by using a computer-controlled INSTRON universal testing machine (Model 5566, Instron Corp., High Wycombe, U.K.). The three-point flexural strengths of sintered rectangular bar specimens (32 mm × 4.0 mm × 3.0 mm) were measured, using a span width of 30 mm and a crosshead speed of 0.5 mm/min (universal testing machine, Model 5566, Instron Corp.).

3. Results and discussion

3.1. Characterization of powder

Fig. 1 shows the XRD patterns of as-prepared HA powder and powder calcined at 900 °C for 2 h. Compared with the standardized card, after calcinations no new phases were detected, but calcined HA powder has a sharper peaks than initial, which means bigger crystalline size and high crystallinity according to Scherrer formular.[26] Chemical analyses indicate that calcined powder have molar ratio Ca/P = 1.695. Fig. 2 shows the particle size distribution of the calcined powder, by sedimentation and light obscuration method, the mean particle size was detected to be 0.44 μm.

3.2. Surface properties of HA powder and its dispersion

Zeta potentials of calcined HA powder at different pH value, dispersed in water containing 1.0 wt% PAA-K or without PAA-

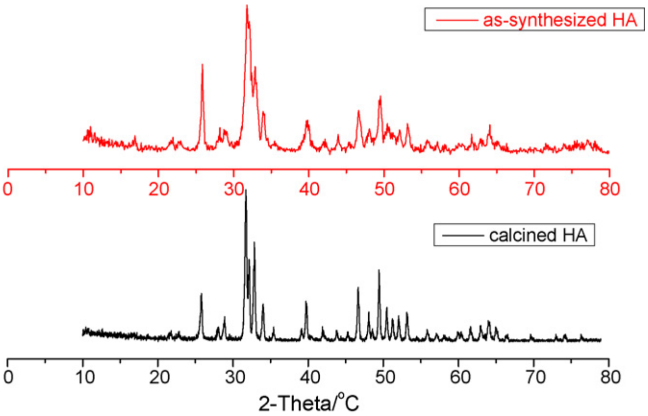

Fig. 1. XRD pattern of as-synthesized and calcined powders.

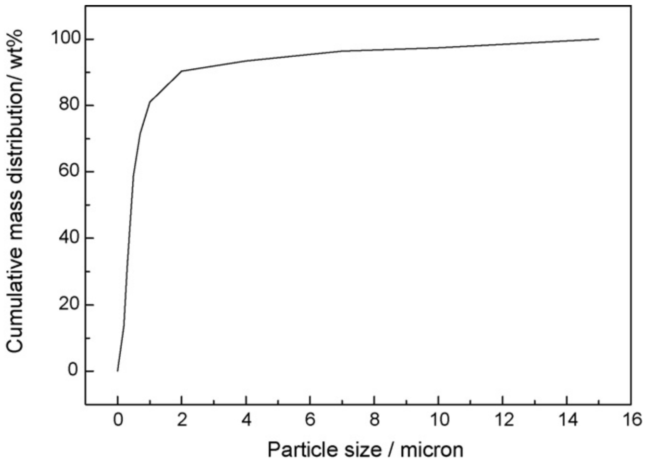

Fig. 2. Particle distribution of the calcined powder.

K, were measured. As shown in Fig. 3, the addition of PAA-K decreased the zeta potential of the powders, which is beneficial for the dispersion of HA particles by electrostatic repulsion. Also, both the zeta potential curves showed an absolute maximum value at pH 11.0.

Viscosity of 45 vol% HA suspensions with different PAA-K contents has been measured at pH 11.0 (Fig. 4). At PAA-K content <1.2 wt% of powder, viscosity of slurry decreases with increasing PAA-K content. In the aqueous medium, the dissociated PAA-K may cover the surface of HA powders and the HA powders would behave as a mono dispersed powder due to the electrosteric stabilization, resulting in a decrease in viscosity of the slurry. At 1.2–1.8 wt% PAA-K, the viscosity changes a little and the minimum viscosity value is observed at 1.6 wt% PAA-K content. This may indicate the adsorbed PAA-K on the surface of the HA powders is enough to prevent HA particle-particle attraction. When the added PAA-K content is higher than the saturated PAA-K absorption point, the free PAA-K would exist in the liquid medium. This may cause inter-locking of PAA-K polymer chain, which bridged the solid particles and caused viscosity increase. Therefore, 1.6 wt% PAA-K was chosen as optimum dispersant amount.

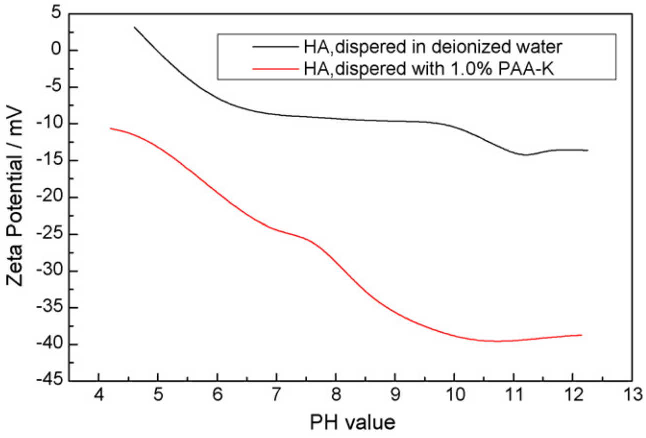

Fig. 3. Zeta potential as a function of pH for HA powder.

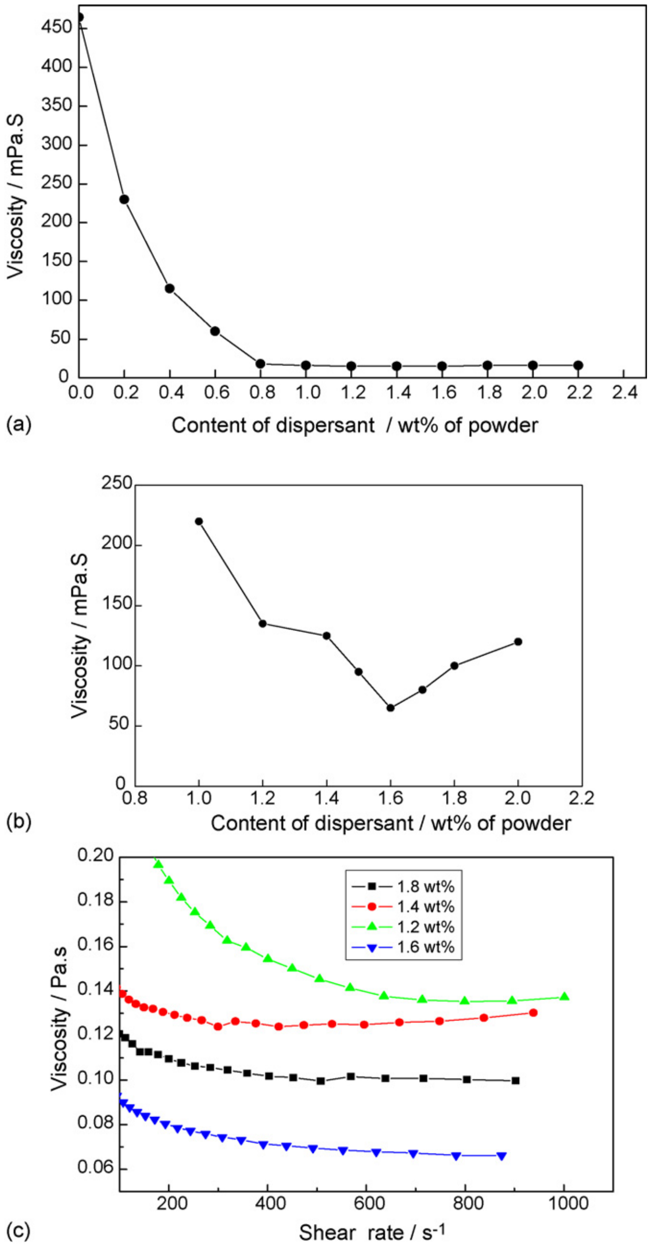

Fig. 4. Influence of dispersant content on the stability of HA slurries: (a) at low solid loading (25 vol%); (b and c) at high solid loading.

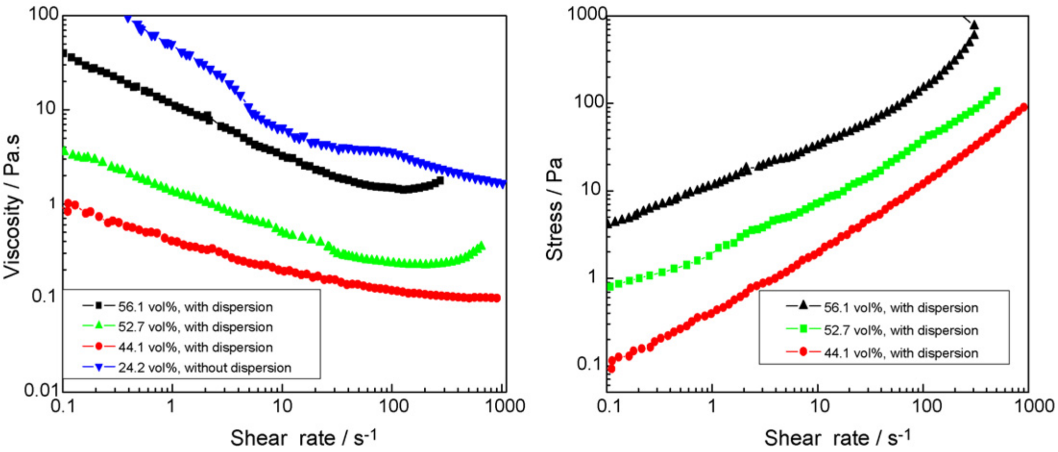

Fig. 5. Rheological curves for the slurries prepared at different HA solid loadings.

3.3. Influence of solid loading

The influence of solid loading on the flow behavior of HA slurry in distilled water is shown in Fig. 5. Shear thinning behavior was observed at solid loading of 24.2–56.1 vol%. And with the increase of the solids loading, the viscosity increased. But, at the same solid loading, the viscosity decreased as shear rate increased. The shear thinning behavior with the shear rate increasing shows that viscosity is strongly dependent on the solid loading. But, when solid loading was above 60.0 vol%, it was difficult to get slurry with well rheological properties in the study. The rheological behavior of HA slurry at 56.1 vol% solid loading has been studied by measuring the viscosity and shear stress at varying shear rates (Fig. 5). As to shear thinning slurries, the relationship between shear stress and shear rate can be described by the Ostwald power law.

$$\tau = KD^n \qquad (1)$$

where τ is the shear stress, D the shear rate, n the shear rate exponent ($n = 1$ refers to a Newtonian fluid) and K is a constant. As shown in Fig. 5, the slip torque versus shear rate curves for 56.1 vol% slurries can be fitted linearly with the correlation coefficients higher than 0.99. The K and n value, which could be obtained from Eq. (1), are 8.45 and 0.60, respectively. Therefore, it is proposed that the 56.1 vol% HA slurries exhibit power law, strong shear thinning behavior, which is universal for stable ceramic slurries. This slurry property meets the requirement for tape casting process.

Table 1
Slurry viscosity and tensile strength of green tape at various *X* ratios

X ratio (binder/powder)	Slurry viscosity (Pa s)	Tensile strength (MPa)
0.04	0.45	Tape cracks
0.06	0.70	1.70 ± 0.03
0.08	0.87	1.95 ± 0.04
0.1	1.12	2.25 ± 0.05
0.12	1.81	1.50 ± 0.05
0.15	2.33	1.15 ± 0.07

3.4. Influence of powder/binder ratio (*X*)

The influence of powder/binder ratio (*X*) was studied (Table 1). Fig. 6 shows the rheological behavior of HA slurry

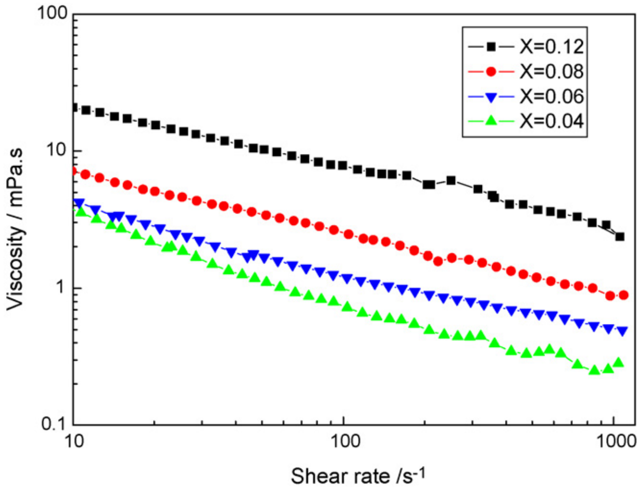

Fig. 6. Rheological curves for the slurries prepared at different *X* ratios.

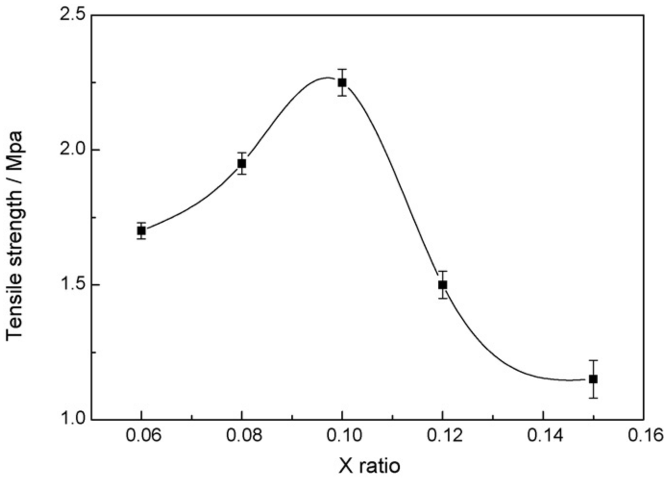

Fig. 7. Tensile strength of green tapes for various *X* ratios.

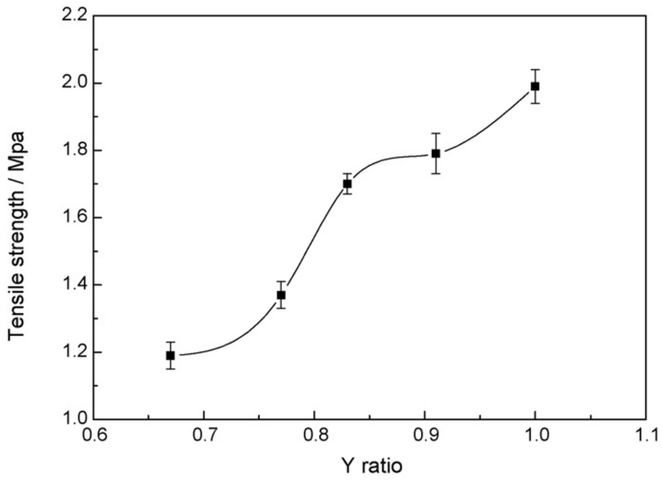

Fig. 8. Tensile strength of green tapes for various *Y* ratios.

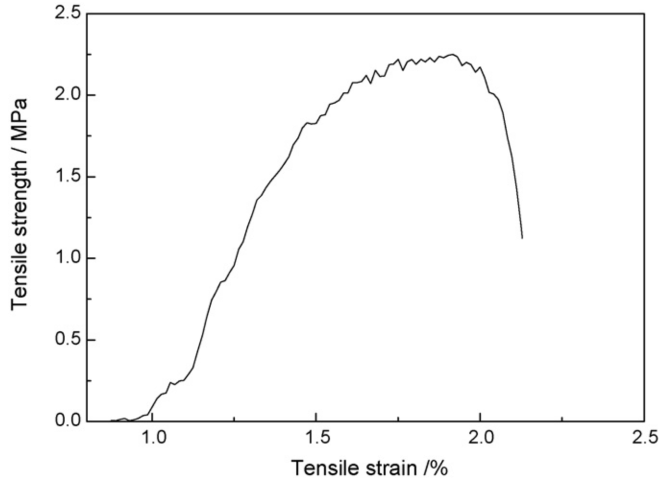

Fig. 9. Stress–strain curve of green tape obtained from tensile strength measurement.

Table 2
Slurry viscosity and tensile strength of green tape at various *Y* ratios

Y ratio (binder/plastisizer)	Slurry viscosity (Pa s)	Tape porosity (vol%)	Tensile strength (MPa)
0.67	0.68	31.53	1.19 ± 0.03
0.77	0.72	28.43	1.37 ± 0.04
0.83	0.77	26.77	1.70 ± 0.03
0.91	0.81	–	1.79 ± 0.06
1	0.97	–	1.99 ± 0.05
1.25	1.06	–	Brittle

at various *X* ratios has been studied by measuring the viscosity at varying shear rates. For the slurries with *X* ratios ranging from 0.06 to 0.15, it was possible to obtain non-cracked green tapes with varying thicknesses. Fig. 7 shows strength curve of green tapes with increasing binder content. There are two possible explanations for this behavior. The first one is that the binder, PVA provides good cohesion of the green tape. The second explanation is that tensile strength is a sensitive indication of the homogeneity of the green tape because failure generally occurs at the critical flaw. At high binder content (high *X* value), the viscosity of the slurry is high and the resultant tape is not homogeneous and subsequently strength is low.

3.5. *Influence of binder/plasticizer ratio (Y)*

In order to study the influence of binder/plasticizer ratio (*Y*), powder/binder ratio (*X*) was fixed to be 0.06. The amounts of binder and plasticizer were adjusted to yield binder/plasticizer ratios ranging from 0.67 to 1.25 (Table 2). Fig. 8 shows that, in the range of Y tested, the viscosity ($\eta = KD^{n-1}$) calculated at a shear rate of 50 s^{-1} increases with increasing binder content. As shown in Fig. 8, tensile strength increases with increasing *Y* ratio. This behavior indicates that the PVA binder exhibits higher strength when unplasticized and has a brittle behavior. Plasticizer reduces the glass transition temperature of the polymer and the viscosity of the suspension. The low molecular weight species of the plasticizer increases the flexibility of the green tape, but at the expense of the tensile strength.

A low *Y* ratio leads to green tapes with higher density and lower porosity than high *Y* ones (Table 2). The low viscosity of the plasticizer-rich organic phase may flow between the ceramic particles and fill the porosity, leading to lowest porosity samples. Particles may also rearrange easily in a low-viscosity organic phase during and immediately after casting.

In addition, according to Greenwood et al.,[27] the flexibility of the final dried tapes was judged by placing the sample on a flat surface and bending one side around a glass rod. If the tape

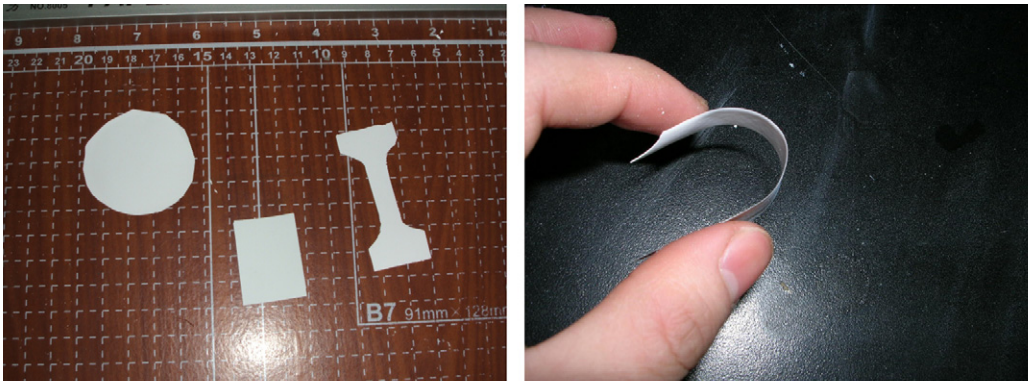

Fig. 10. Clipping and bending of green tapes.

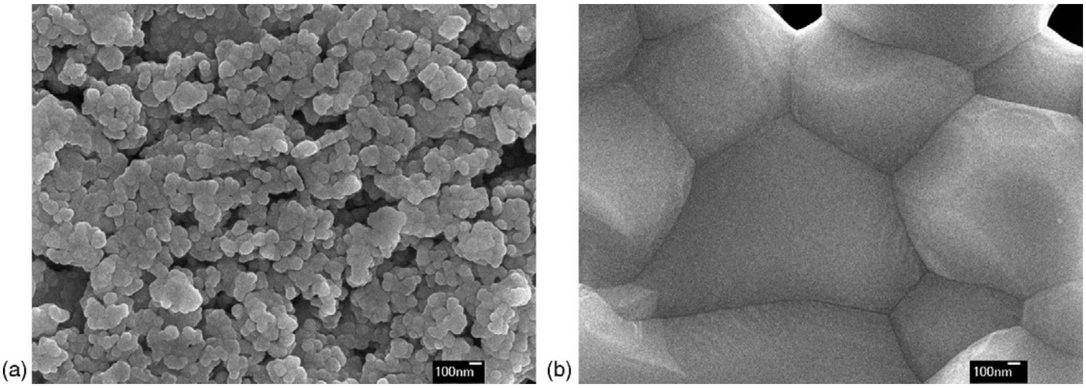

Fig. 11. SEM micrograph of the debindered tape and the sintered sheet: (a) debindered tape; (b) sintered sheet.

Table 3
Properties of HA sintered ceramic

	Density (g/cm^3)	Flexural strength (MPa)	Hardness (GPa)	Elasticity modulus (GPa)
Sintered body ($X = 0.06$; $Y = 0.77$)	3.011 ± 0.005	55.2 ± 6.3	3.54 ± 0.37	88.0 ± 8.5

could be bent through and angle greater than 135°, about 10 times, it was judged to be flexible enough (Figs. 9 and 10).

3.6. Microstructure and mechanical properties of sintered ceramic

Fig. 11 shows the SEM micrographs of the surface of the debindered tape and the sintered sheet. And the mechanical properties of the obtained ceramic were shown in Table 3.

4. Conclusion

The as-synthesized HA powder needs to be previously heat-treated in order to be better dispersed in aqueous system. The solids loading and the dosage of the dispersant (PAA-K) are important factors that determine the rheological behavior and viscosity of the slurries. The optimum dispersant amount, 1.6 wt% of powder, was decided by analysis of the viscosity of slurry. 56.1 vol% HA slurry showed shear thinning behavior nearly without thixotropy, which is suitable for tape casting.

Furthermore, the amounts of binder and plasticizer were decided by detailed rheological analysis and tensile measurement. The desirable slurry with X ratio 0.06 and Y ratio 0.77 was casted, after drying and sintering, the resultant ceramic can be densified to 95.4% (RD) with the flexural strength, elasticity modulus and hardness 55.2 MPa, 88.0 GPa and 3.54 GPa, respectively.

In conclusion, HA sheet with uniform thickness and flexibility could be prepared using a tape casting technique, which has the potential for the fabrication of new types of biomaterials. The biological activities of the apatite sheet, such as cultured cell growth and tissue response will be investigated further.

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