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Factors having influence on the rheological properties of Ti6A14V slurry

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A highly porous Ti6Al4V could be produced with a porous polymeric sponge and Ti6Al4V slurry. However, the rheological properties of Ti6Al4V slurry appeared to be the key issue in the preparation of porous Ti6Al4V. In this study, factors having influence on the rheological properties of Ti6Al4V slurry were addressed in detail. Ti6Al4V powders, organic thickening agents (binders), dispersants, concentration of powder and pH values were optimised with regard to the rheological properties of Ti6Al4V slurry. The results show that Ti6Al4V powder with a mean diameter of 45 μm and spherical shape is beneficial for the preparation of Ti6Al4V slurry. Meanwhile binders with two ingredients, which decompose at different temperatures, have the advantage to keep the shape after debinding. The optimised procedure, based on the findings, made it possible to produce highly porous Ti6Al4V with reticulate porous structure. Porous Ti6Al4V produced by this way is expected to be a promising biomaterial for tissue engineering scaffolds and orthopaedic implant applications.

1. Introduction

In the biomedical field recently, there has been an increasing interest in fabricating porous scaffolds that mimic the structure of human bone, because porous structure allows the ingrowth of new tissue and the transport of the body fluids. For instance, pore characteristics of porous biomaterials are essential for bone grafting materials to achieve good bone in-growth and attachment to tissues. To obtain porous biomaterials that have proper pore size, good morphology and interconnectivity, quite a few methods have been applied. For example, to produce porous calcium phosphate ceramics which have a porous structure similar to that of natural bone, the following methods have been addressed: (1) duplicating a coral skeleton [1, 2]; (2) keeping the bovine cancellous bone structure [3, 4]; (3) foaming ceramics from slurry [5, 6]; (4) freeze-drying an aqueous slurry [7]; (5) impregnating a porous polymeric sponge which is subsequently pyrolysed [8]. Among the methods mentioned, the last method is quite often used. Compared with other methods, this method can easily generate an open, 3-D porous structure, which is similar to that of human cancellous bone. However, this method requires a good knowledge of the rheological properties of slurry.

Although porous calcium phosphate ceramics are good bone graft substitutes because of their osteoconductive and even osteoinductive property [9–12], their inherently low mechanical strength limits their applications to non-load-bearing sites. For bone repair or replacement in load-bearing sites, such as vertebral fusion, porous biomaterials with good mechanical properties are needed, and thus development of porous metals becomes an important aspect in biomaterial science for hard tissue repair or replacement.

In the past years, titanium and its alloy have been widely used as implant materials under load-bearing conditions in orthopaedics and dental implantology because of their low modulus, superior biocompatibility and corrosion resistance [13]. Due to the importance of porous structure of biomaterials in hard tissue replacement, titanium or its alloy has also been produced in porous forms. These are widely used in biomedical prostheses [14], such as hip joint and dental implant coating, etc. In general, porous titanium or its alloy could be produced by traditional powder metallurgical technique, such as sintering loose powder, powder compact and fibre pressing [15–20]. However, since porous metals made by such methods have a low porosity ($< 45\%$) and a pore size depending on the particle shape and size, porous metals obtained by these methods are not comparable to human cancellous bone that has a porosity of about 75% and a pore size from 100 to 600 μm.

To improve the porosity and porous structure of porous titanium or its alloy, the method of polymeric sponge replication was first introduced to make porous Ti6Al4V [21]. Earlier, this method was used to make porous CaP ceramics as discussed in several publications [22–24],

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TABLE I Chemical composition of Ti6Al4V powder

Element (wt %)	Al	V	N	H	O	C	Fe	Si	Ti
TC4P2-325	6.47	4.08	0.025	0.008	0.183	0.02	0.12	0.04	Bal
TC4P2-200	6.47	4.09	0.025	0.008	0.175	0.02	0.12	0.04	Bal
TC4-325	6.5	4.2	0.04	0.01	0.20	0.05	0.2	0.04	Bal
ISO5832	5.5–6.8	3.5–4.5	0.05	0.015	0.20	0.08	0.3	0.04	Bal

but there are no reports in the literature as to how to use this method for porous Ti6Al4V. The procedure itself is simple. Ti6Al4V slurry prepared from Ti6Al4V powders and binders was coated onto a polymeric foam, thereafter the foam construction was subjected to drying, pyrolysing, and sintering with a special process to remove polymeric foam and binders. After a final sintering at a high temperature and high vacuum, a porous Ti6Al4V was produced. Two key steps are included to produce porous Ti6Al4V: preparation of Ti6Al4V slurry and removal of foam struts and final sintering. The rheological behaviour of slurry becomes the most important parameter in doing so. It is, therefore, of great practical importance to achieve good rheological characterisation of slurry to coat the uniform Ti6Al4V slurry on the foam struts and to keep the sponge's shape after the removal of sponge struts.

The objective of this work is to study the influence on the rheological behaviour of Ti6Al4V slurry. (a) Particle size, particle morphologies and their distributions, (b) kinds and contents of the binders and dispersants, (c) other relevant variables such as powder concentration, pH value, air bubbles, and at the end, to achieve Ti6Al4V slurry, which is suitable to make porous Ti6Al4V with porosity and pore size similar to those of human cancellous bone.

2. Materials and methods

2.1. Raw materials

Three commercially available Ti6Al4V powders were employed in this study. These are TC4P2-325, TC4P2-200 [Bongen Titanium (China) Co. Ltd] and TC4-325 [China Baoji Titanium Powder Factory]. The chemical composition of Ti6Al4V powders are listed in Table I as compared with the ISO5832 standard requirements.

Other materials used in this study are polyethylene glycol1500 (PEG1500; Fluka Chemie GmbH, Germany), polyethylene glycol4000 (PEG4000; Fluka Chemie GmbH, Germany), methylcellulose (MC; Fisher Scientific BV, The Netherlands), ammonia (25% ammonia solution, Merck), 1-octanol (Acros Organics, USA), dolipix (Aschimmer and Schwarz GmbH, Germany) and polyethylene foam 3.31R45 (Calligen Europe BV, The Netherlands).

The shape of different Ti6Al4V powders was analysed under environmental scanning electron microscope (ESEM; XL-30, Philips, Eindhoven, The Netherlands). Particle sizes were measured with the working principle of incoherent light diffraction (Crystalizer®).

Thermogravimetrical analyses (TGA; Perkin Elmer, software of Pyris windows) were performed on PEG4000 and MC in order to find out their thermal behaviour.

2.2. General analysis methods

Sediment speed: Sedimentation of different Ti6Al4V slurries was tested in volumetric flasks with the same volume. The initial level (L1) of slurry was recorded, after an interval time, the level (L2) of slurry was recorded. The speed of sediment was indicated as $\Delta L/\Delta T$, where $\Delta L = \mathrm{L1} - \mathrm{L2}$

Viscosity: The rheological behaviour of Ti6Al4V slurries was measured at room temperature by viscometer (Brookfield Engineering Labs DV-II + viscometer) with interval time at a speed of 20 rpm with a RV5 spindle.

pH Value: The pH value of slurry was measured at room temperature by a pH metre (Portamess PHM 85, Knick, Germany).

2.3. Experimental procedures

The Ti6Al4V slurry served as a model to study the influence of Ti6Al4V powder (particle size, particle shape and concentrations), binders (type and concentration), dispersant, pH value and air bubbles.

The components of Ti6Al4V slurries for different purposes varied but were prepared in a similar way. First, demineralized water was mixed with binders by stirring for 1 h, Ti6Al4V powder were subsequently added to the solution and stirred for 1.5 h. Then Dolapix, ammonia solution and 1-octanol may be added to the slurry and stirring was maintained for 1 h to obtain the final Ti6Al4V slurry.

2.3.1. Influence of Ti6Al4V powders on rheological behaviour

The influence of Ti6Al4V powders on rheological behaviour of their slurries was characterised by measuring sediment speed and viscosities of different Ti6Al4V slurries with 70 wt % powders (TC4P2-325, TC4P2-200, TC4-200) and 2 wt % MC in water.

2.3.2. Influence of type and concentration binders on rheological behaviour

First, the viscosities of PEG1500, PEG4000 and methylcellulose were tested in 2 wt % aqueous solutions. Then the influences of PEG1500, PEG4000 and methylcellulose were tested in Ti6Al4V slurries with 70 wt % powder (TC4P2-325), 1 wt % dolapix, 1 wt % ammonia, 1 wt % 1-octanol, 2 wt % of PEG1500, PEG4000 and methylcellulose separately with regard to the viscosities. Finally, the influence of PEG4000 and MC concentrations on the viscosities of Ti6Al4V slurries were tested on the Ti6Al4V slurries with 70 wt % powder (TC4P2-325), 1 wt % dolapix, 1 wt % ammonia, 1 wt % 1-octanol and different concentration of PEG4000 and MC, respectively.

2.3.3. *Influence of concentration of powder on rheological behaviour*

The influence of Ti6Al4V powder concentration on the viscosity of Ti6Al4V slurry was investigated on the slurries with 50–85 wt % powder (TC4P2-325), 3.0 wt % PEG4000, 0.5 wt % MC, 1.0 wt % dolapix, 1.0 wt % ammonia and 1.0 wt % 1-octanol.

2.3.4. *Influence of dispersant on rheological behaviour*

The influence of dispersant (Dolapix) concentrations on the viscosity of Ti6Al4V slurry was tested on the slurry containing 75 wt % Ti6Al4V powder (TC4P2-325), 3.0 wt % PEG4000, 0.5 wt % MC, 1.0 wt % ammonia, 1.0 wt % 1-octanol and Dolapix at concentrations from 0.25 to 2.0 wt %.

2.3.5. *Influence of pH value on rheological behaviour*

To test the influence of pH value on the viscosity of Ti6Al4V slurry, ammonia was dropped into the slurry with 75 wt % powder (TC4P2-325), 1.0 wt % dolapix, 1.0 wt % 1-octanol and 2 wt % PEG4000 to adjust the pH value and meanwhile viscosity and sediment speed of slurry were measured.

2.3.6. *Influence of air bubbles*

Three different methods were used to eliminate bubbles: (1) static curing, (2) chemicals removal and (3) vibration. Experiments were performed on the slurry with 75 wt % Ti6Al4V powder (TC4P2-325), 3.0 wt % PEG4000, 0.5 wt % MC, 1.0 wt % Dolapix and 1 wt % ammonia. The viscosity of slurry with/without air bubbles was measured.

2.3.7. *Preparation of a porous Ti6Al4V*

Optimised slurry was obtained with regard to the components in Table II, and a porous Ti6Al4V was made of such optimised slurries. First, polyurethane foam was dipped into the slurry. The dipping process was repeated until all the struts of the PU foam were coated with Ti6Al4V slurry. The extra slurry was then removed by using a pressing-rolling to achieve a well-distributed coating on the foam. Thereafter the raw porous body was first dried for 3 hrs. at 80 °C and then for 24 hrs. at room temperature. Subsequently, the samples were heated to burn out foam (50 °C/h to 500 °C under flow argon) and sintered in high vacuum furnace at 1250 °C with holding time of 2 h. The porous Ti6Al4V body was observed with ESEM.

TABLE II Chemical composition of Ti6Al4V slurry

Ingredient	Wt %
Demi water	18.5
PEG4000	3.0
Dolapix	1.0
Ammonia	1.0
Methylcellulose	0.5
1-octanol	1.0
Ti powder	75.0

3. Results

3.1. Powder shape and size

Under ESEM, Ti6Al4V powders showed different particle shapes and sizes (Fig. 1). Both TC4P2-325 and TC4P2-200 particles are spherical, but TC4P2-200 has a bigger particle size than those of TC4P2-325 and TC4-325. TC4-325 is similar to TC4P2-325 in particle size but has an irregular shape. Particle size distribution of

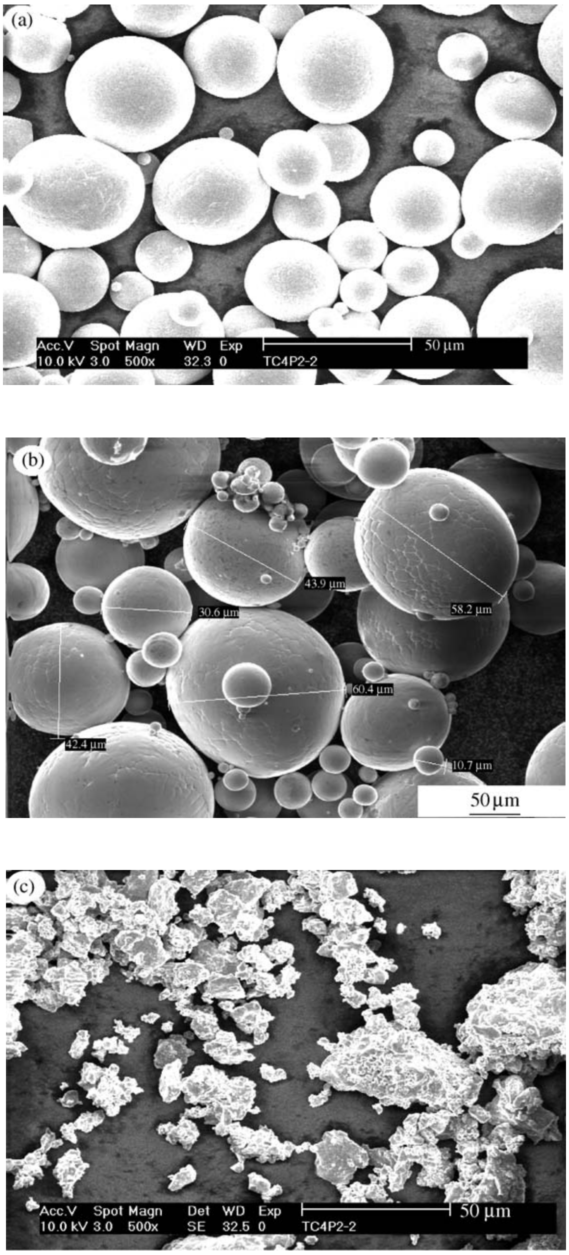

Figure 1 Particle shape and size of Ti6Al4V powders under ESEM (a) TC4P2-325; (b) TC4P2-200; (c) TC4-325.

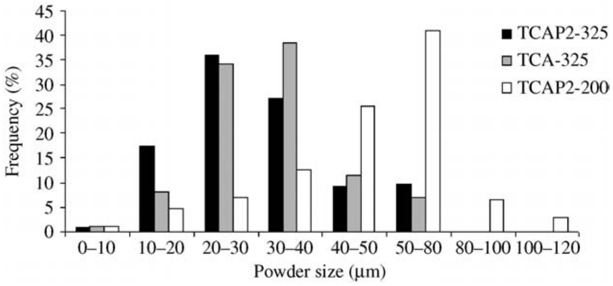

Figure 2 Size distributions of Ti6Al4V particles in different powders.

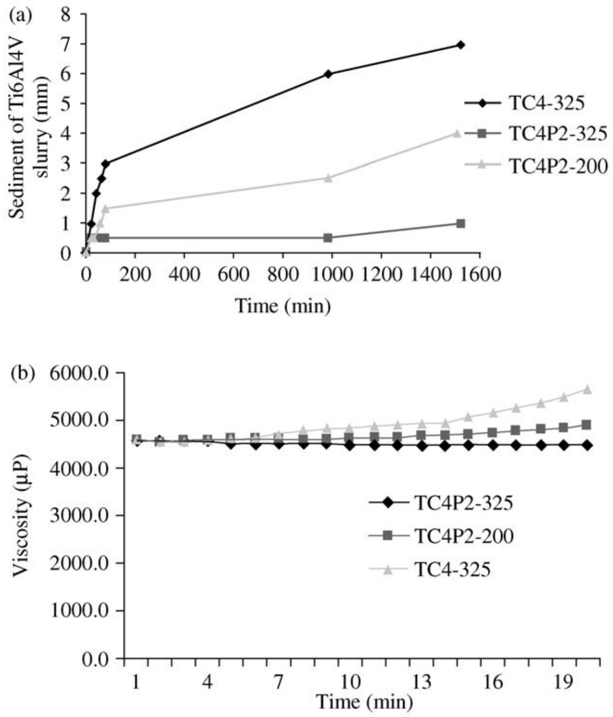

Figure 3 Influence of Ti6Al4V powder types on the rheological properties of titanium alloy slurries: (a) Sediment of Ti6Al4V powders with time in the slurries having 70 wt %powder, and 2.0 wt % MC; (b) Influence of powders on the viscosity of Ti6Al4V slurries (70 wt % powder, 1.0 wt % MC) as the function of time.

Ti6Al4V powders is shown in Fig. 2. The majority of TC4P2-325 and TC4-325 size (∼ 72%) is between 20 and 40 μm, while the majority of TC4P2-200 size (∼ 66%) is between 40 and 80 μm. The particle size of TC4P2-325 and TC4-325 are almost the same, but the particle size of TC4P2-200 is bigger than that of TC4P2-325 and TC4-325.

The sediment speed of three kinds of slurries is displayed in Fig. 3(a), and the viscosity of different Ti6Al4V slurries is shown in Fig. 3(b). Considering different Ti6Al4V slurries, no significant difference in viscosity was observed, but their sediment speed were significantly different. TC4-325 sediments is faster than TC4P2-200 than TC4P2-325.

3.2. Influence of the binders

The viscosities of PEG1500, PEG4000 and methylcellulose aqueous solution (2.0 wt %) were shown in Fig. 4(a). It was shown that with the same concentration (2.0 wt %) of PEG1500, PEG4000 and methylcellulose, methylcellulose aqueous solution has much higher viscosity than PEG1500 and PEG4000. Although PEG1500 and PEG4000 aqueous solutions have a similar viscosity in water, they behave differently in Ti6Al4V slurry. As shown in Fig. 4(b), different binders in the same Ti6Al4V slurry resulted in different viscosity of the slurries. Ti6Al4V slurry with MC still has a higher viscosity than the slurries with PEG1500 or PEG4000. Obviously and most importantly, the viscosity of Ti6Al4V slurry with PEG1500 was not stable and increased with time.

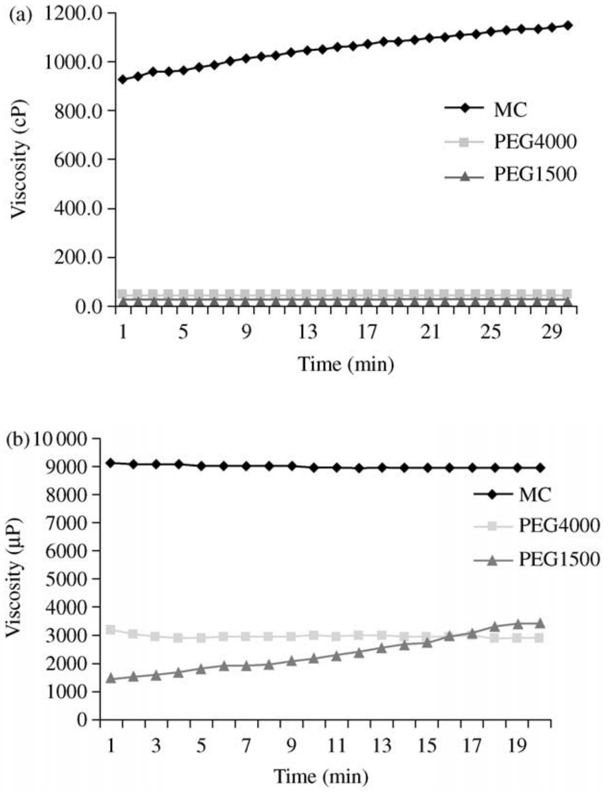

Figure 4 Influence of binders on the viscosity of Ti6Al4V slurries: (a) Viscosities of PEG1500, PEG4000 and methylcellulose aqueous solution (2.0 wt % in water); (b) Influence of binders on the viscosity of Ti6Al4V slurries (2.0 wt % binder MC, 70 wt % TC4P2-325 powder, 1.0 wt % Dolapix, 1.0 wt % ammonia and 1.0 wt % octanol).

The binders first adjust the viscosity of the Ti6Al4V slurry to obtain suitable slurries, and second help to keep the shape of the green bodies, but at the end they were debinded at a high temperature. Fig. 5 showed that decomposition of PEG4000 and MC under nitrogen. PEG4000 started to decompose at 150 °C and MC started to decompose at 300 °C.

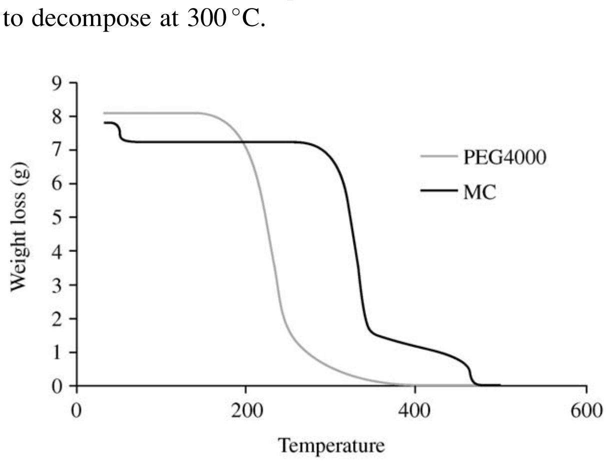

Figure 5 TGA curves of PEG4000 and MC.

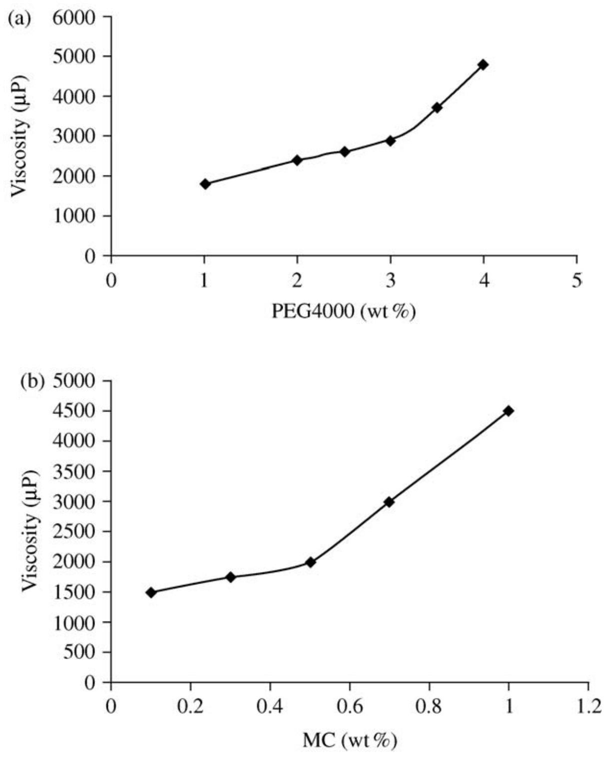

Figure 6 Influence of binder concentration on the viscosity of Ti6Al4V slurry (70 wt % TC4P2-325 powder, 1.0 wt % Dolapix, 1.0 wt % ammonia and 1.0 wt % octanol) varied with different the amount of binder. (a) PEG4000; (b) MC.

Not only the types of the binders, but also the concentrations will influence the Ti6Al4V slurries. The viscosity of Ti6Al4V slurry increased with both PEG4000 (Fig. 6(a)) and MC (Fig. 6(b)).

3.3. Powder concentration

In addition to the particle shape and particle size, the concentration of the Ti6Al4V powder in the slurries influences the viscosity: the higher the powder concentration, the higher the viscosity (Fig. 7). The viscosity of the Ti6Al4V slurry increased slightly from 50 to 75 wt % TC4P2-325, but increased sharply when concentration was above 75 wt %.

3.4. Dispersant

Fig. 8 shows the viscosity versus the amount of dispersant (Dolapix). A concentration of approximately 1.0 wt % Dolapix allowed the achievement of slurries containing 75 wt % powder with the lowest viscosity. Further increase of Dolapix increased the slurry viscosity.

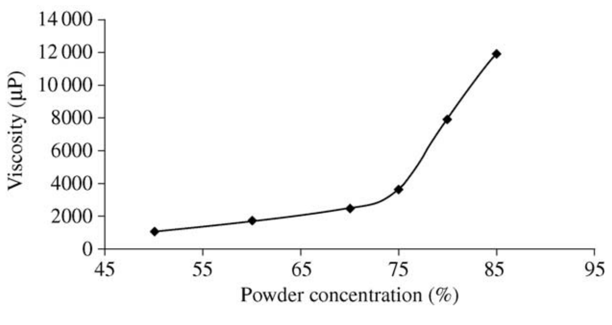

Figure 7 Change of the viscosity of Ti6Al4V slurry with TC4P2-325 powder concentration (3.0 wt % PEG4000 and 0.5% MC, 1.0 wt % Dolapix, 1.0 wt % ammonia and 1.0 wt % octanol).

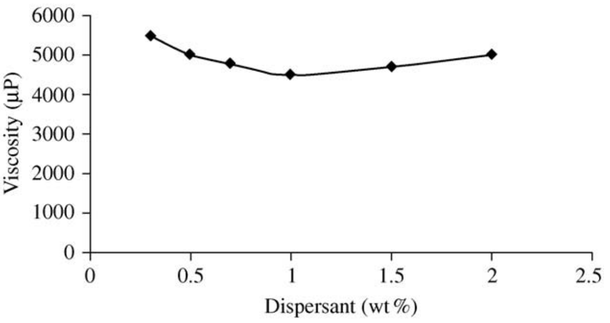

Figure 8 Viscosity of Ti6Al4Vslurry as function of dispersant (Dolapix) concentrations (75 wt %TC4P2-325 powder, 3.0 wt % PEG4000 and 0.5%MC, 1.0 wt % ammonia and 1 wt % octanol).

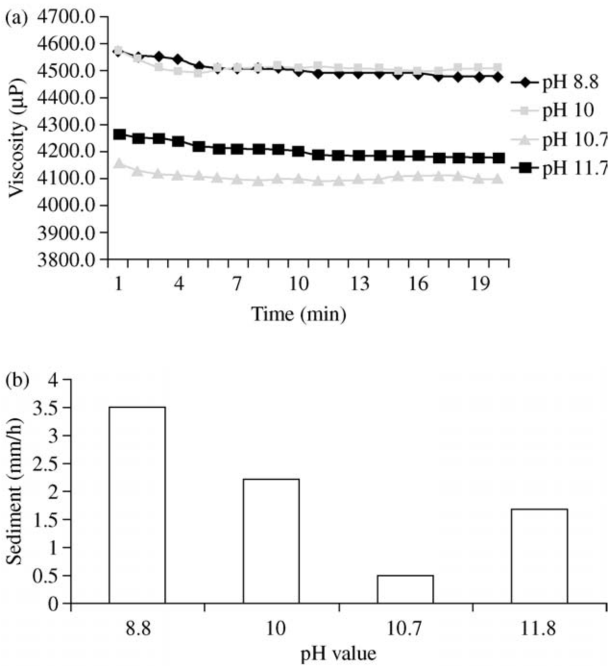

Figure 9 Influence of pH value: (a) viscosity of Ti6Al4V slurry with different pH as the function of time (75 wt %TC4P2-325 powder, 3.0 wt % PEG4000 and 0.5%MC, 1.0 wt % ammonia and 1.0 wt % octanol); (b) sediment speed of Ti6Al4V slurry with different pH.

3.5. pH value

The pH of the slurry also influences the viscosity and the sediment speed of Ti6Al4V slurry (Fig. 9). The viscosity remains stable between pH 8–10, decreases sometimes with further increase of the pH, while the slurry with a pH value of 10.7 has the lowest viscosity (Fig. 9(a)). The influence of pH on sediment speed was not in one tendency, low agglomeration occurs at pH 10.7 in the Ti6Al4V slurry (Fig. 9(b)).

3.6. Air bubbles

The existence of air bubbles in slurry is detrimental to coat Ti6Al4V slurry on struts of foam and results in a variety of microstructure defects such as cracks, pores on the wall and other large flaws. Table III shows air bubbles are affected by different treatments. Chemical removal is

TABLE III Air bubbles corresponding procedures of treatment and time

Method	Time 10 min	30 min	60 min
Static curing	+ + +	+ +	+
Vibration	+ +	+	−
Chemical	+	−	−

" + + + ": A lot of air bubbles on the surface; " + + ": some of air bubbles; " + ": a few of air bubbles; " − ": no air bubbles were seen on the surface

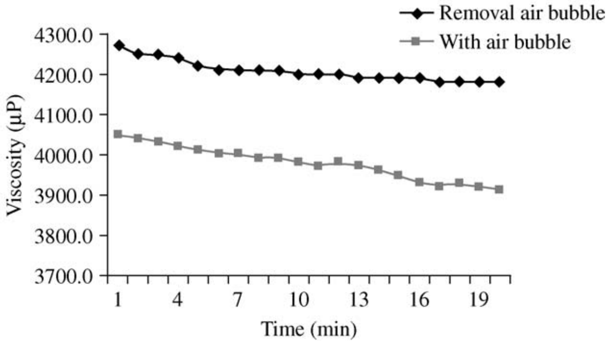

Figure 10 Change of the viscosity of Ti6Al4V slurry with the removal of air bubbles as the function of time (75 wt% TC4P2-325 powder, 3.0 wt% PEG4000 and 0.5% MC, 1.0 wt% ammonia and 1.0 wt% octanol).

an effective method, followed by vibration. Static curing is not an effective one, as a few air bubbles are still found on the surface of slurry after 1 h static curing.

The influence of air bubbles on the viscosity of slurry is shown in Fig. 10. The viscosity of slurry is slightly higher after removal of air bubbles.

3.7. Porous Ti6Al4V

Fig. 11 showed the structure of porous Ti6Al4V fabricated with a polymeric sponge and optimised Ti6Al4V slurry. The porous structure was similar to that of the original polymeric sponge with interconnected pores.

4. Discussion

Slurry preparation, debinding and final sintering are the key steps in the preparation of porous Ti6Al4V by polymeric sponge replication. The rheological behaviour of Ti6Al4V slurry is a key in the preparation of suitable Ti6Al4V slurry, similar to already published articles concerning the rheological behaviour of different calcium phosphate ceramic slurries [25–27]. In general, the Ti6Al4V slurry must be fluid enough to enter, fill and uniformly coat the sponge network and subsequently remain sufficiently viscous so as to adhere on the struts. The viscosity is an important parameter to characterize the rheological behaviour of Ti6Al4V slurry. When viscosity is high, the slurry is sticky and it is difficult to flow and to remove extra slurry after impregnation of sponge to achieve homogenous coating. On the other hand, if the viscosity of the slurry is low, the slurry is thin and only limited amounts of Ti6Al4V is coated on the struts, with the consequence that it is subsequently difficult to maintain the shape of the green porous Ti6Al4V body after the sponge foam is burned out.

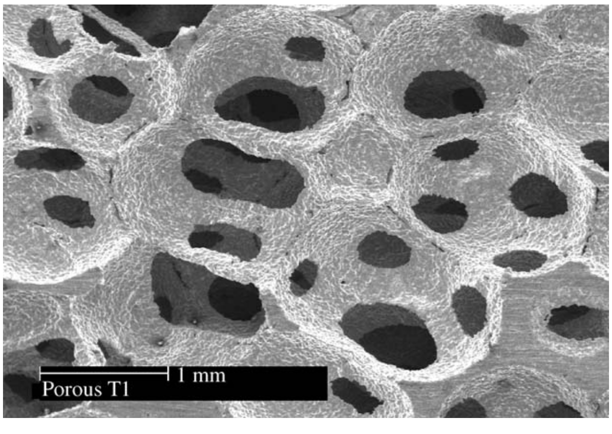

Figure 11 Porous Ti6Al4V as observed under ESEM.

In order to obtain suitable Ti6Al4V slurry to make a porous Ti6Al4V, factors that have influences on Ti6Al4V slurry were studied step by step in this study.

4.1. Ti6Al4V powders

Ti6Al4V powder was found to be one of the important factors having influence on the rheological behaviour of Ti6Al4V slurry. Three Ti6Al4V powders were tested, and they performed differently. First, the sediment speed differed for each powder, TC4-325 deposited in the slurry quicker than TC4P2-200, while TC4P2-325 deposited slower than other two Ti6Al4V powders in the slurry (Fig. 3(a)). Second, the viscosity changed differently with powders. The viscosity of TC4-325 slurry increased with time, so did the viscosity of TC4P2-200 slurry, although not as quickly as the viscosity of TC4-325 slurry. However, the viscosity of TC4P2-325 slurry remained stable with time (Fig. 3(b)). The performance of different powders in slurries was caused by their particle shape and size. Having smaller particle size and similar particle size distribution (Fig. 2), but different particle shape, TC4-325 and TC4P2-325 had different sediment speed. Having irregular particle shapes (Fig. 1(c)), TC4-325 deposited in the slurry fast, but having spherical shape (Fig. 1(a)), TC4P2-325 deposited in the slurry slowly (Fig. 3(a)). The particle shape affected not only the sediment speed of the powders in the slurry but also the viscosity of the slurry. The spherical particle shape was helpful to keep the viscosity of the slurry stable with time, as compared the viscosity of TC4-325 slurry and TC4P2-325 slurry (Fig. 3(b)). Although the spherical particle shape was in general useful in slurry preparation, the particle size was still a matter. Having same particle shape as TC4P2-325 (Fig. 1(a) and (b)), but bigger particle size (Fig. 2) TC4P2-200 deposited faster than TC4P2-325 (Fig. 3(a)). Meanwhile, the viscosity of TC4P2-200 slurry (having big particle size) increased with time (Fig. 3(b)). Having spherical particle shape and small particle size, TC4P2-325 deposited in slurry slowly and the viscosity of its slurry remained almost stable with time. Since stable Ti6Al4V slurry is what is being looked for, TC4P2-325 was chosen as a standard powder to analyse other factors and for future use. Besides the particle shape, particle size and size distributions, Ti6Al4V powders influence their slurries with their concentrations, as shown in Fig. 7, the viscosity increased with TC4P2-325 powder, slowly from 50 to 75 wt %, but sharply when TC4P2-325 powder was more than 75 wt %.

4.2. Binders

Careful selection of Ti6Al4V powder was important but not enough for Ti6Al4V slurry preparation, binders, which in one hand to allow Ti6Al4V powder suspend in the slurry and further adjust the rheological behaviour (namely the viscosity) of the slurry on the other hand, were needed. It is clear that the binders should be carefully selected. The binders should not react chemically to Ti6Al4V powder and could be removed from green body without contamination of porous Ti6Al4V body. Meanwhile, the binders should adjust the viscosity of Ti6Al4V slurry to suitable degree. Three materials were tested as binders with the TC4P2-325 slurry. At the same concentrations, MC aqueous solution had a high viscosity, while PEG1500 and PEG4000 aqueous solution had low viscosity separately (Fig. 4(a)). Not only in the aqueous solutions, same trend was found in Ti6Al4V slurry. At the same concentration, MC gave higher viscosity than PEG1500 and PEG4000 in the Ti6Al4V slurry (Fig. 4(b)). Differently but most importantly, the viscosity of the Ti6Al4V slurry with MC and PEG4000 remained stable with time, but the viscosity of the Ti6Al4V slurry with PEG1500 increased with time (Fig. 4(b)). The results suggested the influence of binder types on the rheological behaviour of Ti6Al4V slurry. Since PEG1500 resulted in un-stable Ti6Al4V slurry, it was therefore not a good binder material and may not be used in the preparation of Ti6Al4V slurry. Binders influenced the rheological behaviour of Ti6Al4V slurry with both their types and their concentrations. As shown in Fig. 6, the viscosity of Ti6Al4V slurry increased with the concentrations of both MC (Fig. 6(a)) and PEG4000 (Fig. 6(b)).

4.3. Dispersant, pH value and air bubbles

Besides Ti6Al4V powders and binders, dispersant materials were used in the preparation of Ti6Al4V slurry in order to prevent the aggregation of Ti6Al4V particles and therefore to achieve a homogenous Ti6Al4V slurry. Dolapix was often used as a dispersant in slurry preparation [28, 29]. Dolapix influenced the viscosity of Ti6Al4V slurry with its concentrations (Fig. 8). A concentration of 1.0 wt % dolapix resulted in lower viscosity, as compared with more or less concentration of dolapix.

It is known that pH helps the fluidity of slurries for slip casting [30]. In this study, ammonia was used to adjust the pH of Ti6Al4V slurry. The viscosity of slurry varied with different pH value (shown in Fig. 9(a)). The slurry has the lowest speed of sediment when pH value is about 10.7 (shown in Fig. 9(b)). The reasons may be given as follows. Normally, Ti6Al4V powder has an oxide surface layer. In an aqueous solution, the oxide surface of Ti6Al4V powder released OH^-, which gives a rise to a net surface charge. According to the theory of the electrical double layer [31], the zeta potential surrounding the Ti6Al4V particles increased with the increase of pH due to increased surface charge density, and hence the repulse force between particles increased. Thereafter, less agglomeration occurred in the slurry with the decrease of viscosity.

Besides the fluidity of the Ti6Al4V slurry, air bubbles have impact on the homogeneity of the final slurry coating on the porous forms. Some study showed that the air bubble would affect the density of slurry [32]. Our experiment shows that the viscosity of slurry was influenced by air bubbles as well. Viscosity of the slurry increased with removal of air bubbles (Fig. 10). Keeping the influence of Ti6Al4V powders, binders, dispersant, pH and air bubbles in mind, Ti6Al4V slurry was optimised with a concentration of 75 wt % TC4P2-325 powder, 3.0 wt % PEG4000 and 0.5 wt % MC, 1.0 wt % dispersant, 1.0 wt % ammonia and 1.0 wt % 1-octanol. This slurry was homogeneous without any clusters of particles, had a stable viscosity of 3000–5000 uP, a pH value of 10.5, and did not have obvious air bubbles. It had a good rheological behaviour for the impregnation of sponge. When sponge was dipped into slurry and the extra slurry could be easily removed by press rolling to achieve distribute coating. After debinding and sintering the porous Ti6Al4V with sponge structures was successfully obtained (Fig. 11). In general, the optimisation of the slurry was mainly based on the rheological behaviour of Ti6Al4V slurry, but on the other hand, some factors, which having possible influence on the properties of the final porous Ti6Al4V, were also taken into account in the optimisation. Powder with spherical shape and small size was selected for use. On the one hand, this kind of powder gave good rheological behaviour of the slurry; on the other hand, by providing relatively large surface area, this powder ensured a higher powder concentration (75 wt %) as compared to other metals slurry such as stainless steel (60 wt %) [33], and may eventually give a higher mechanical strength of the final porous Ti6Al4V, because of a high concentration of powder in the slurry, more powder could be coated. Furthermore, the small particle may easily create microstructures on the macropore surface which may be helpful to improve the biological performance of the porous Ti6Al4V [11, 12].

It should be noted that titanium or Ti6Al4V is a very reactive metal and can react with nitrogen, oxygen and carbon to form titanium compounds. The formation of titanium compounds would affect sintering of porous Ti6Al4V and the mechanical strength of the final porous Ti6Al4V. So, binders, dispersant and other components in the slurry should be used carefully to avoid any chemical reactions. The most likely cause of compound formation is debinding, the removal of the binders. Removal of binder is usually carried out by solvent or thermal extraction methods. Considering the process of porous Ti6Al4V, besides the removal of binders, the foam had to be removed from green body at same time, so the thermal extraction was selected as a debinding method. For the thermal extraction, usually it is effective to remove binders and foam, but it is easy to generate carbon residue and other compounds due to chemical reaction [34]. Several groups have reported the way in which a polymer degrades under heating in an inert atmosphere [35,36]. The thermal decomposition of a polymer is explained by a chain depolymerisation and a random decomposition [37]. It is suggested that binders, which are pyrolysed by the mechanism of a chain depolymerisation, are used to reduce the impurity content [37]. Low-density polyethylene is decomposed by a chain depolymerisation. It can be seen by TGA result, during debinding stage, PEG4000 and MC first debinded at 150 °C and 300 °C respectively, after heating above 500 °C, only little PEG4000 and MC were left and therefore reduced the possibility to form possible compound in the final sintering at a high temperature (1250 °C). PEG4000 and MC, as binders, on the one hand, reduced the possible compound formation, on the other hand, due to their different decomposition temperature, PEG4000 and MC helped to keep the shape of the green body. Because PEG4000 first decomposed and then MC as a binder was still left to remain the original shape of the green body under the high temperature.

5. Conclusion

By studying the influences of Ti6Al4V powders, binders, dispersant, pH value and air bubbles on the rheological behaviour of Ti6Al4V slurry, Ti6Al4V slurry was optimised as a composition of 75 wt% Ti6Al4V powder (TC4P2-325), 3.0 wt% PEG4000, 0.5 wt% MC, 1.0 wt% Dolapix, 1 wt% ammonium solution and 1 wt% 1-octanol. By using the optimised Ti6Al4V slurry, a porous Ti6Al4V was successfully produced by the impregnation of polymeric sponge.

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