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Effect of surface modification of β-tricalcium phosphate on mechanical properties of poly(L-lactic acid) composites

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In this study, in order to improve interfacial strength between β-tricalcium phosphate (β-TCP) and poly(L-lactic acid) (PLLA), the surfaces of β-TCP were modified. L-lactic acid was used for an interfacial treatment agent, and effects of the amount of L-lactic acid on mechanical properties of the composites were examined. β-TCP/PLLA compound was obtained by kneading and specimens were fabricated by hot-pressing. Mechanical properties of composites were investigated by tensile testing and fracture toughness testing. The composite with β-TCP treated using 6% L-lactic acid per 100 g β-TCP showed improved tensile strength and fracture toughness.

Keywords: bioabsorbable composites; poly(L-lactic acid); β-tricalcium phosphate; interfacial treatment

1. Introduction

The conventional metallic implants have been used for fracture repair and support in the oral surgery, orthopedic surgery, and thoracic surgery because of their high strength and high wear resistance. However, the usage of these implants is not totally without problems. For example, in order to avoid bone resorption caused by stress shielding due to high elastic modulus of metal and fatigue failure caused by corrosion or inflammation owing to metal elution, metallic materials should be removed from body after complete recovery.

As a bone fixation material, poly(L-lactic acid) (PLLA) have attracted wide attentions for their biodegradability in human body. On the other hand, comparing with modulus and strength of cortical bone, 17 GPa and 131 MPa, mechanical properties of PLLA are not sufficient. Therefore, in order to improve stiffness and strength, combinations of PLLA with bioactive ceramic filler with higher elastic modulus, such as hydroxyapatite (HA) or tricalcium phosphate (TCP), have been investigated.[1–3]

Stiffness of bioactive ceramics/PLLA composite is improved with increasing filler content, whereas strength becomes lower due to the lower interfacial strength between PLLA and the fillers. For improvement of interfacial strength, surface treatments on filler particles have been conducted.

In order to improve the affinity of filler to matrix, surface modifications of filler with coupling agent have been conducted. Table 1 summarizes the previous results. Dong et al. grafted hexamethylene diisocyanate (HMDI) on calcium hydrogen

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Table 1. Previous investigations about modification of bioactive filler materials.

	Filler	Modifier	Test method	Result
[4]	HA	HMDI	Thermal gravimetric analysis	Improved
[5]	HA	Dodecyl alcohol	Colloid stability (in alcohol)	65 days (1–7 days)[a]
[6]	HA	VPA	Colloid Stability (in water)	Improved
[7]	HA	EGMP	Colloid Stability (in water)	Improved
[8]	HA	PEG and HMDI	–	–[b]
[9]	HA	Tetraethyl orthosilicate	Colloid stability (in water) Acid environment	Improved Prevent of degradation of HA

[a]The values in brackets are result of non-treated filler materials.
[b]Just confirmation of grafting.

phosphate.[4] Nicholas et al. esterified surface of HA using dodecyl alcohol to improve colloidal stability.[5] Choi et al. improved surface of HA nanocrystals using vinyl phosphonic acid (VPA) and confirmed improved colloidal stability in water.[6]. Lee et al. grafted ethylene glycol methacrylate phosphate (EGMP) on the surface of thiolated HA.[7] They reported that the grafted HA crystals did not aggregate and presented dramatically improved colloidal stability in water. Liu et al. obtained poly(ethylene glycol) (PEG) grafted HA with HMDI as a coupling agent.[8] Borum et al. coated Si on HA through hydrolysis of tetraethyl orthosilicate.[9] In the case of Si concentration 50 wt.%, HA presents not only colloidal stability but antioxidation property in acidic environment.

Investigations about composites using surface modified filler were summarized in Table 2. Liu et al. grafted PLLA on surface of bioactive glass (BG) and reported mechanical properties of the composite with modified BG was improved.[10] As investigations with similar method, Li et al. [11] and Hong et al. [12] modified HA surface through the route of ring-opening polymerization of lactic acid (LA). Qiu et al.

Table 2. Previous investigations about mechanical characterization of bioresorbable composite reinforced with modified filler materials.

	Filler	Modifier	Matrix	Filler content (wt.%)	Test method	Result	
[10]	BG	PLLA	PLLA	4	Tensile test	Strength	70 MPa (55 MPa)
[11]	HA	LA	PLLA	5	Tensile test	Strength	55 MPa (45 MPa)
[12]	HA	L-Lactide	PLLA	8, 10	Tensile test	Elongation	10% (4%)
					Tensile test	Strength	58 MPa (52.5 MPa)
[13]	HA	L-lactic acid oligomer	PLLA	15	Tensile test	Strength	68 MPa (57 MPa)
	HA	L-lactic acid	PLLA	10	Tensile test	Strength	65 MPa (50 MPa)
						Elongation	44% (6.5%)
	HA	L-lactide	PLLA	10		Strength	68 MPa (50 MPa)
[14]	HA	L-lactic acid Oligomer	PLGA	20	Three-point Bending test	Strength	4.1 MPa (2.5 MPa)
					Compressive test	Strength	2.3 MPa (0.8 MPa)
[15]	HA	PCL	PCL	20	Tensile test	Strength	70 MPa (52 MPa)
[16]	TCP	LA or CL with phosphoric acid	Poly (L, DL- lactide)	25	Tensile test	Strength	52.2 MPa (73.2 MPa)
						Elongation	3.4% (3.6%)

Note: The values in brackets are result of non-treated filler/matrix composites.

modified HA with LA oligomer or through ring-opening polymerization route and reported that mechanical properties were improved with HA modified by polymerization of LA.[13] They used PLLA as a matrix material. Cui et al. used poly (glycol-co-lactic acid) and HA particles modified with LA oligomer.[14] Wang et al. developed PCL reinforced with HA grafted with PCL.[15] As for modification of TCP which has more resorbable properties in body than HA, Kunze et al. conducted surface modification with LA or ε-caprolactone monomer (CL) after surface activation with phosphoric acid.[16] From the fracture surface observation, improved adhesion between TCP and matrix was confirmed. However, improvement in composite strength was not obtained.

In this study, we selected β-TCP, PLLA, and LA as filler, matrix, and surface treatment agent, respectively, because higher resorbable property of β-TCP and higher biosafeness of PLLA and LA. Effects of the amount of surface treatment agent on mechanical properties of β-TCP/PLLA composites were investigated and the optimum condition on improvement of mechanical properties was revealed.

2. Method

2.1. *Surface treatment of β-TCP particles*

Materials used are β-TCP powder (Rasa Koei Co., Japan), PLLA pellet (Lacty #5000, Shimadzu, Japan), and lactic acid (Wako Chemical Co., Japan). In order to improve interfacial strength between PLLA and β-TCP, β-TCP surface was treated with L-lactic acid solution.

First, measured amount of L-lactic acid was added to 300 ml purified water. Then 200 g β-TCP was dispersed to L-lactic acid solution. The suspension was stirred with a magnetic stirrer and evaporated in a hot water bath for 3 h. These were followed by drying in an oven at 80 °C. After water was removed completely, β-TCP treated with L-lactic acid was sieved. In order to examine the effects of amount of L-lactic acid on mechanical properties of the composites, the amount of L-lactic acid was varied as 6, 9, 12, 15, or 24 g. In the present study, modified β-TCP was labeled as LA amount per 100 g β-TCP, i.e. β-TCP treated with 6, 9, 12, 15, and 24 g as β-TCP-3, 4.5, 6, 7.5, and 12%, respectively.

2.2. *Thermal gravimetric analysis*

Thermal gravimetric analysis (TGA) was conducted to determine the amount of L-lactic acid on β-TCP surface. Measurement was conducted from room temperature to 700 °C at a rate of 5 °C/min under air atmosphere using a differential thermal and thermogravimetric analyzer (DTG-60, Shimadzu Co., Japan). Measurements were conducted on non-treated and interfacially treated β-TCP particles. The amount of L-lactic acid on β-TCP surface was calculated as a difference between weight loss of non-treated β-TCP and that of interfacially treated β-TCP. The ratio of interphase thickness to β-TCP grain size (*t*/*r*) was decided according to the following equation:

$$\frac{t}{r} = \frac{1}{3} \frac{\rho_{\beta-\mathrm{TCP}}}{\rho_{L-\mathrm{lactic\,acid}}} \frac{W_{L-\mathrm{lactic\,acid}}}{W_{\beta-\mathrm{TCP}}} \tag{1}$$

where t is interphase thickness and r is β-TCP grain size. $\rho_{\beta\text{-TCP}}$ and $\rho_{\text{L-lactic acid}}$ are densities of β-TCP and L-lactic acid, respectively. $W_{\beta\text{-TCP}}$ and $W_{\text{L-lactic acid}}$ are weights of β-TCP and L-lactic acid, respectively.

2.3. pH measurement

pH measurement was used to determine the amount of L-lactic acid on β-TCP surface.

First, 5 g β-TCP was dispersed in purified water of 30 ml. Then the suspension was left for 24 h. The pH value of the suspension was measured by a pH meter. Hydrogen-ion concentration ([H$^+$] [mol/l]) of the suspension was calculated using the pH value and following equation.

$$[\mathrm{H}^+] = 10^{-x}, \quad x = \mathrm{pH} \tag{2}$$

Since L-lactic acid was weak acid, L-lactic acid molecules would not ionize in the suspension. Thus, concentration of L-lactic acid (c [mol/l]) in suspension was calculated by concentration of hydrogen-ions as shown in the following equation.

$$[\mathrm{H}^+] = c\alpha = \sqrt{cK_a} \tag{3}$$

where α is ionization degree ($\alpha \ll 1$) and K_a is ionization constant.

2.4. Preparation of β-TCP/PLLA composites

Non-treated and surface-modified β-TCP/PLLA compounds were obtained by kneading. β-TCP/PLLA composite compounds with β-TCP content of 15 wt.% and 30 wt.% were prepared. PLLA and β-TCP were kneaded at 200 °C and at 50 rpm for 20 min with a batch-type mixer (IMC-1882, Imoto Co. Japan).

Compounds obtained were crushed into small pieces with a mill (SM-1, AS One Co., Japan). Then the crushed compounds were molded into composite plates by hot-pressing. The mixtures were re-melted at 200 °C for 20 min, and then pressed for 5 min. After cooling to 30 °C, a composite plate was obtained.

2.5. Crystallinity measurement

Crystallinities of specimens were measured with differential scanning calorimeter (DSC) (DSC-60, Shimadzu Co., Ltd., Kyoto, Japan). DSC samples were cut out from the injection-molded specimens with a weight of 3–6 mg. The samples were heated with a heating rate of 5 °C/min up to 220 °C in the air. The crystallinity of a PLLA sample (X_{c1}) was calculated as follows

$$X_{c1} = \frac{\Delta H_m + \Delta H_c}{\Delta H_{100\%}} \times 100 \tag{4}$$

where ΔH_c is the crystallization enthalpy, ΔH_m and $\Delta H_{100\%}$ are the enthalpy of melting of a PLLA sample and PLLA crystal having infinite crystal thickness. We used 135 J/g as $\Delta H_{100\%}$.[17]

The crystallinity of a TCP/PLLA composite sample (X_{c2}) was calculated as follows

$$X_{c2} = \frac{\Delta H_{\mathrm{composite}}}{\Delta H_{100\%}} \times \frac{M_c}{M_m} \times 100 \tag{5}$$

where M_c is the weight of TCP/PLLA composite, $\Delta H_{\mathrm{composite}}$ is the enthalpy of melting of a TCP/PLLA composite sample.

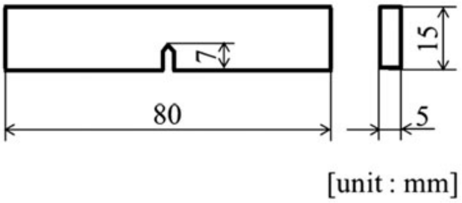

Figure 1. Geometry of fracture toughness test specimen.

2.6. *Tensile test*

Specimen geometry for tensile test was 100 mm × 10 mm × 3 mm. Aluminum tabs were glued on both ends of specimens for preventing stress concentration. Strain gauges (KFG-2, Kyowa Co., Japan) were also glued on the center of both surfaces of specimens to monitor strain during tests. The tensile test was carried out with a universal testing machine (AG-1000A, Shimadzu Co., Japan) at room temperature. The crosshead speed was 1 mm/min.

2.7. *Fracture toughness test*

Single-edge-notch-bending (SENB) specimens were fabricated from composite plates for mode I fracture toughness testing. The geometry of the SENB specimen is shown in Figure 1. The mode I fracture toughness tests on SENB specimens were carried out on a three-point bending test fixture with a universal testing machine (AG-IS 50kN, Shimadzu Co., Japan) at room temperature. The crosshead speed was 0.1 mm/min. The mode I critical stress intensity factor K_{IC} was calculated by following equations.

$$K_{IC} = f(x)\frac{P_C}{BW^{1/2}}, \quad x = a/W \tag{6}$$

$$f(x) = \frac{6x^{1/2}}{(1+2x)(1-x)^{3/2}}\lfloor 1.99 - x(1-x)(2.15 - 3.93x - 2.7x^2)\rfloor$$

where P_C is the critical load. The critical load corresponds with the initiation of nonlinearity on load-time curves. B and W are the thickness and width of specimen, respectively, and $f(x)$ the geometrical correction factor.

3. Analytical characterization

3.1. *Molecular orbital calculation*

In this study, L-lactic acid was used for surface treatment on β-TCP. In order to examine characteristics of L-lactic acid molecule, molecular orbital calculation was conducted using a semi-empirical quantum chemistry software (WinMOPAC Version3.0.3, Fujitsu Co., Japan), which can predict chemical characteristics and modeling chemical reaction for a molecular constructed on this software.

3.2. *Surface electric charge of β-TCP*

It was known that Ca atoms were charged positively on β-TCP surface.[18] Thus, we calculated the number of Ca atoms on β-TCP surface using particle radius, crystal

Table 3. Material properties of β-TCP.

Chemical formula	β-$Ca_3(PO_4)_2$
Crystal system	Rhombohedral crystal
Lattice constant	a : 1.04391 nm b : 3.73756 nm
Density	3.067 g/cm^3
Radius of β-TCP	1.94 μm

lattice constant, and density of β-TCP as shown in Table 3. First, the number of crystal lattice was determined using average radius of a β-TCP particle, lattice constants, and crystal system of β-TCP. Then, considering the sizes of the crystal lattice and L-lactic acid molecule, the number of Ca atoms where L-lactic acid molecules can adsorb was calculated. Finally, the number of Ca atoms existing on β-TCP surface and the number of L-lactic acid molecules were determined and compared.

4. Experimental result

4.1. Thermal gravimetric analysis

Figure 2 shows the weight loss of β-TCP particles. The amount of L-lactic acid on β-TCP surface increased with increasing L-lactic acid used for interfacial treatment. Relationship between *t*/*r* and the amount of L-lactic acid was shown in Figure 3. *t*/*r* increased approximately linearly with increasing amount of L-lactic acid. In the present study, at most 5% of interphase thickness was obtained.

4.2. pH measurements

Figure 4 shows result of pH measurement of aqueous solutions including non-treated and interfacially treated β-TCP. The pH of purified water was 7.07. The pH value of suspension including non-treated β-TCP was lower than purified water because of ionization of β-TCP. The pH of suspension including interfacially treated β-TCP decreased with increasing the amount of L-lactic acid. Since L-lactic acid was weak acid, L-lactic

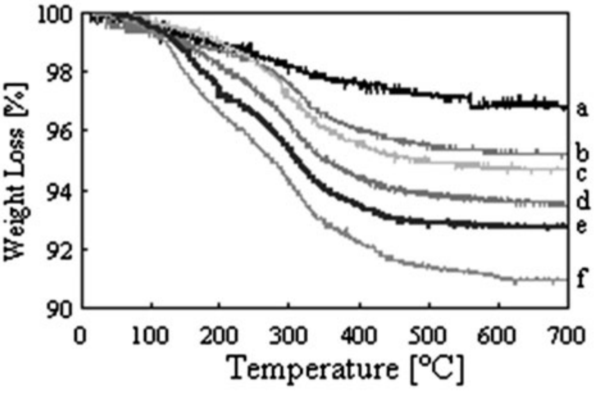

Figure 2. TGA curves of (a) non-treated β-TCP and β-TCP treated with L-lactic acid (b) 3%, (c) 4.5%, (d) 6%, (e) 7.5%, and (f) 12%.

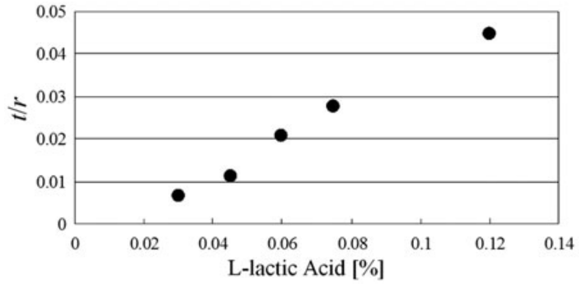

Figure 3. Relationship between *t/r* and the amount of L-lactic acid.

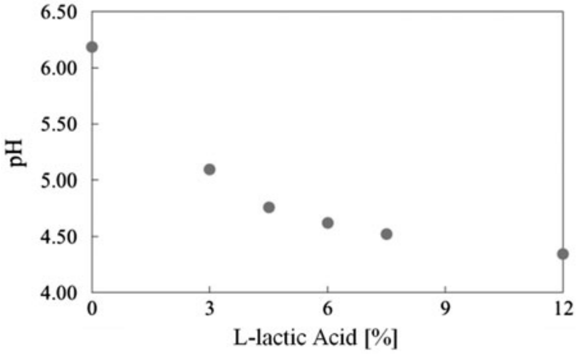

Figure 4. pH value on each β-TCP solutions.

acid adhered to β-TCP surface ionized in aqueous water. Therefore, suspension including interfacially treated β-TCP presented lower pH value than that including non-treated β-TCP.

Using result of pH measurement and Equation (2), hydrogen-ion concentration of each suspension was calculated. As a possibility, a part of hydrogen-ion involving in interfacial-treated β-TCP suspension was not from L-lactic acid but from β-TCP. Thus, hydrogen-ion concentration from L-lactic acid molecules was defined as a difference between interfacially treated β-TCP suspension and hydrogen-ion concentration of non-treated β-TCP suspension. Figure 5 shows the result. Hydrogen-ion concentration linearly increased with increasing L-lactic acid.

Using Hydrogen-ion concentration obtained and Equation (3), concentration of L-lactic acid in suspension, c was calculated and shows in Table 4. The acid dissociation constant of L-lactic acid used was $pK_a = 3.8$.[19] As shown in Table 4, L-lactic acid concentration was lower than hydrogen-ion concentration. It was contrary to the definition that degree of ionization is equal to or lower than unity. It seemed that β-TCP affects ionization of L-lactic acid. In the suspension, not only hydrogen ions that ionized from L-lactic acid but also calcium ions or phosphoric ions that ionized from β-TCP exist. Since calcium hydroxide is strong base, calcium ion does not bond to hydroxide ion. On the other hand, hydrogen phosphate is middle acid. Thus, phosphoric ions might bond to hydrogen ions. It was thought that in solution including β-TCP,

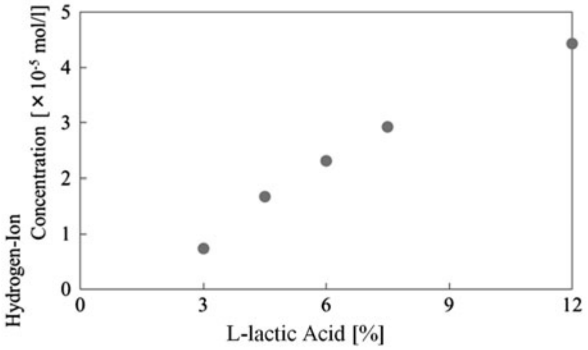

Figure 5. Concentration of hydrogen ions.

Table 4. Concentrations of hydrogen ions and L-lactic acid.

	[H+] [$\times 10^{-5}$ mol/l]	c [$\times 10^{-6}$ mol/l]	c' [$\times 10^{-5}$ mol/l]
3 phr	0.74	0.35	0.87
4.5 phr	1.67	1.77	4.43
6 phr	2.32	3.37	8.50
7.5 phr	2.93	5.42	13.6
12 phr	4.43	12.4	31.2

ionization degree become lower compared with the case of including L-lactic acid only. Therefore, ionization constant was shifted from 3.8 to 5.2 so that L-lactic acid concentration becomes higher than hydrogen-ion concentration. The modified L-lactic acid concentration, c', was also shown in Table 4. The precious values for L-lactic acid concentration are unclear. However, the values c' in Table 4 provide rough estimations for them.

4.3. *Crystallinity measurements*

Figure 6 shows relationship between crystallinity of PLLA matrix and amount of L-lactic acid. Crystallinity slightly increased with increasing β-TCP content from 15 to 30 wt.% and amount of L-lactic acid. These results suggest that β-TCP particles and L-lactic acid on the surface of β-TCP particles act as nuclei which accelerate crystallization. In our previous study, range of crystallinity from 15 to 25% did not affect strength of matrix.[20] Thus, this range of crystallinity has no effect on strength of composites.

4.4. *Tensile tests*

Figure 7 shows tensile strength of non-treated and treated β-TCP/PLLA composites with 15 and 30 wt.% β-TCP contents. For all composites, tensile strength decreased with increasing β-TCP contents. For both β-TCP content of 15 and 30 wt.%, strength of the β-TCP-3% and β-TCP-4.5% composites were comparable with that of composites with non-treated β-TCP. The β-TCP-6% composites exhibited maximum tensile

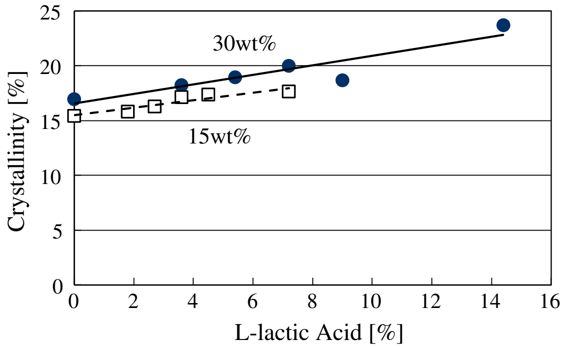

Figure 6. Crystallinity of PLLA in β-TCP/PLLA composites.

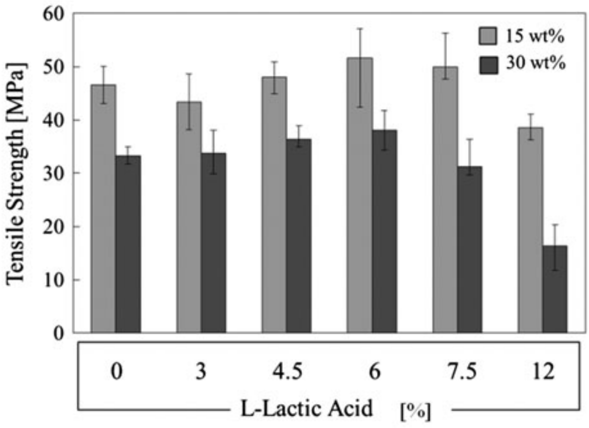

Figure 7. Tensile strength of β-TCP/PLLA composites.

strength. This result suggested that β-TCP surface treatment using 6% L-lactic acid was optimum for improvement of interfacial strength. On the other hand, tensile strength of β-TCP-12% composite was much lower than that of non-treated composites.

Figure 8 shows elastic modulus of non-treated and interfacially treated β-TCP/PLLA composites with 15 and 30 wt.% β-TCP contents. Elastic modulus increased with increasing β-TCP content from 15 to 30 wt.%, because elastic modulus of β-TCP was much higher than that of PLLA matrix. However, little differences in moduli were observed between the composites with non-treated and treated β-TCP, regardless of amount of LA. Therefore, it was found that there is no effect of interfacial treatment on the elastic modulus.

Figure 9 shows fracture surface for TCP/PLLA composites after tensile tests observed by scanning electron microscopy. Fracture surface indicated failure occurred in a brittle manner from macroscopic observation. From the result of microscopic observation, it is clarified that fracture surface consisted of two types of region, such as flat and brittle region and ductile region where void formed. Figure 10 shows the ratio of ductile area to whole area of fracture surface. Ductile region is narrow for

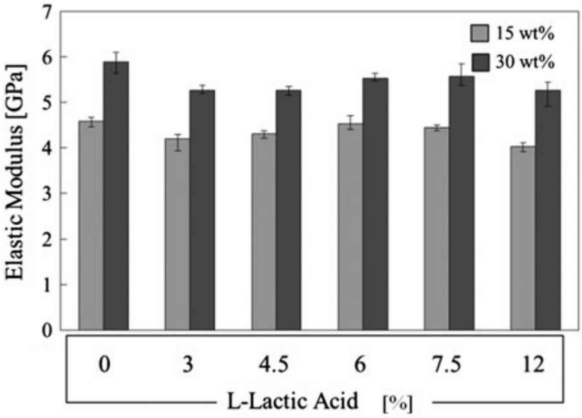

Figure 8. Elastic modulus of β-TCP/PLLA composites.

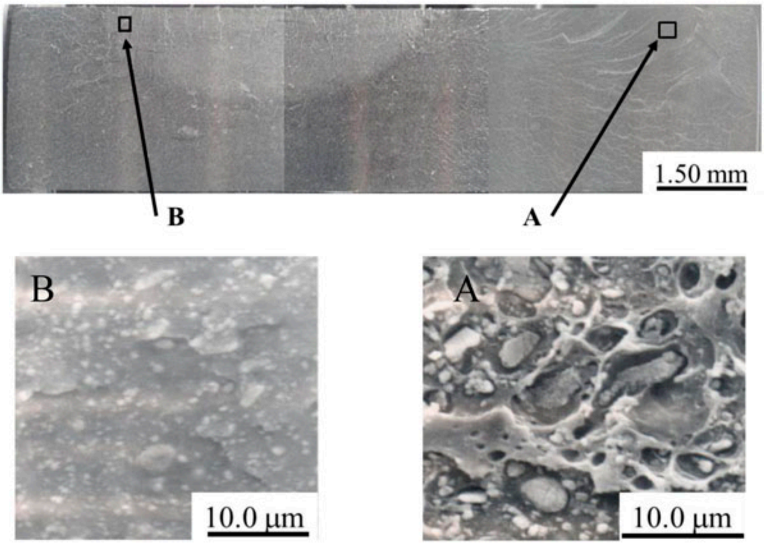

Figure 9. Fracture surface for 30wt% β-TCP-4.5%/ PLLA composite after tensile tests.

non-treated specimen. This is due to lower interfacial strength which results in earlier interfacial debonding followed by rapid growth of matrix crack without void formation. In the interfacially treated composites, stress was enough for immediate void formation when interfacial debonding onset.

4.5. Fracture toughness tests

Figure 11 shows fracture toughness of non-treated and interfacially treated β-TCP/PLLA composites. Fracture toughness of neat PLLA was 2.9 MPa m$^{1/2}$. Fracture toughness of β-TCP/PLLA composites significantly decreased with β-TCP content. For β-TCP content of 15 wt.%, the composites with treated β-TCP indicated higher fracture

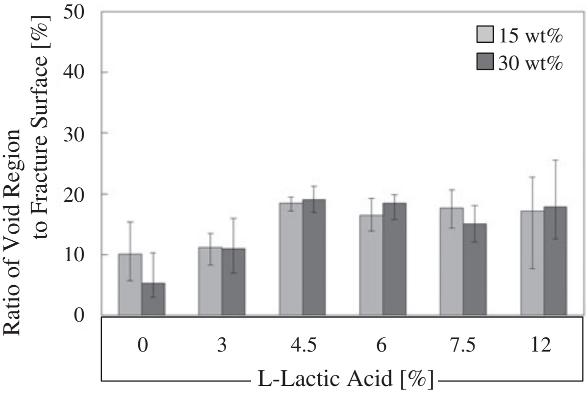

Figure 10. Ratio of void formation area to whole area of fracture surface.

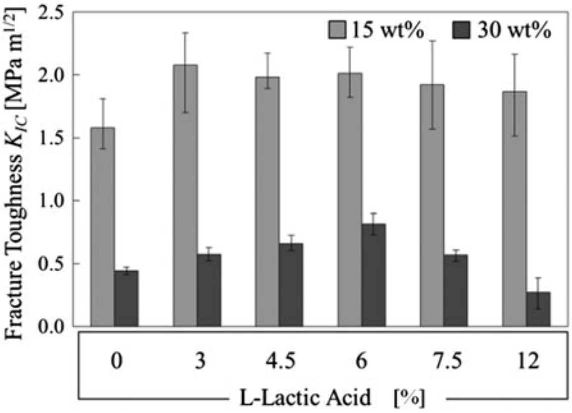

Figure 11. Fracture toughness of β-TCP/PLLA composites.

toughness than non-treated β-TCP/PLLA. And there is no effect of the amount of L-lactic on fracture toughness of the composites with treated β-TCP.

For β-TCP content of 30 wt.%, the β-TCP-12% composite showed lower fracture toughness than non-treated composite, whereas other composites with treated β-TCP showed higher fracture toughness. The β-TCP-6% composite has highest fracture toughness. This is similar tendency with tensile strength.

4.6. Evaluation on method of interfacial treatment

Figure 12 shows charge density distribution of L-lactic acid obtained by molecular orbital calculation. In L-lactic acid, oxygen atom (O) which was doubly bonded to carbon atom (C) exists. It was thought that electrostatic interaction works between O atom negatively charged in L-lactic acid and Ca atom positively charged on β-TCP surface. In addition, H atom in the end of L-lactic acid binds to hydroxyl group of PLLA where

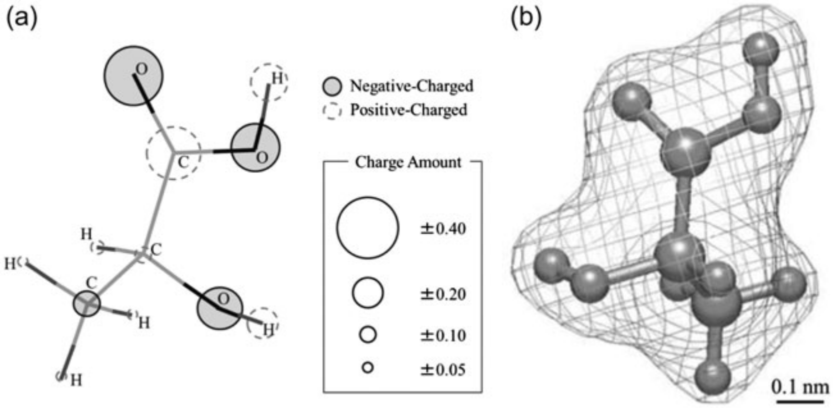

Figure 12. Molecular structure of (a) charge density distribution L-lactic acid and (b) electron orbit of L-lactic acid.

Table 5. The number of Ca and L-lactic acid molecules.

β-TCP (phr)	The number of Ca	The number of L-lactic acid
3	1.15×10^{18}	0.16×10^{18}
4.5		0.80×10^{18}
6		1.54×10^{18}
7.5		2.47×10^{18}
12		5.66×10^{18}

polar interaction works between L-lactic acid and PLLA and dehydration occurs, which result in the improvement of interfacial strength.

The number of Ca atoms on β-TCP surface was calculated from β-TCP surface area, crystal lattice surface area, and so on. Considering the diameter of L-lactic acid molecules calculated by molecular simulation (about 6.2 Å, as shown in Figure 10), the number of Ca atoms that L-lactic acid could be bonded to without overlapping was determined to be eight per one particle. Total number of Ca atoms available to bond to L-lactic acid and the number of L-lactic acid molecules in suspension was also calculated with molecular weight, Avogadro constant and L-lactic acid concentration, *c*'. These results are shown in Table 5.

β-TCP treated with 6% L-lactic acid presents good agreement between the number of L-lactic acid molecules and Ca atoms. This result indicates that 6% L-lactic acid treatment is optimum. In the case of lower amount of L-lactic acid, shortage of L-lactic acid bound to Ca atom results in physical adhesion of PLLA to β-TCP and lower interfacial strength. On the other hand, in the case of higher amount of L-lactic acid, successive L-lactic acid remains on the surface of β-TCP not to bind. Thus, PLLA do not bind to β-TCP, which results in lower interfacial strength.

5. Conclusion

In this study, in order to improve interfacial strength of β-TCP/PLLA, β-TCP surface was modified with L-lactic acid. The optimum condition of interfacial treatment was investigated. β-TCP/PLLA compound was obtained by kneading and fabricated by hot-pressing. Mechanical properties were studied by tensile test and fracture toughness test. From the results of tensile test, both β-TCP content of 15 and 30 wt.%, β-TCP-6% composite showed highest tensile strength. On the other hand, tensile strength of β-TCP-12% composite decreased significantly. From the results of fracture toughness test with lower β-TCP content, interfacial treatment improved fracture toughness, whereas with higher β-TCP content, fracture toughness was affected by the amount of L-lactic acid and β-TCP-6wt% composite indicated the highest fracture toughness. The amount of L-lactic acid bound to β-TCP surface was determined with pH value of suspension. From result of pH measurement, hydrogen-ion concentration of suspension increased linearly with increasing L-lactic acid from 3 to 12%. Considering β-TCP crystal structure and from molecular orbital calculation, in the case of using β-TCP treated using L-lactic acid 6%, L-lactic acid molecules were bonded to Ca atoms on β-TCP surface in just proportion. Thus, it is suggested that surface treatment with 6% L-lactic acid improved surface strength effectively.

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