

Properties and Morphology of Bioceramics/Poly(D,L-lactide) Composites Modified by *In Situ* Compatibilizing Extrusion

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ABSTRACT: Composites of poly(D,L-lactide) (PDLLA) with hydroxylapatite (HA) and PDLLA with tertiary calcium phosphate (TCP) were prepared by *in situ* modification with methylenediphenyl diisocyanate (MDI) and molded by piston extrusion at temperature between T_g and T_m of PDLLA. Mechanical properties of the composites increased obviously when compared with the unmodified bioactive ceramic particles/PDLLA composites. The effect of MDI contents on mechanical properties of the composites was studied. At the optimum conditions of 1.0/1.0 molar ratios of —NCO groups in MDI to —OH groups in PDLLA, bending strength 68.4 MPa and bending modulus 2281.5 MPa, were achieved in composite HA/PDLLA/MDI with 15 wt % HA. Both increased by nearly 30% when compared with that of solution cast HA/PDLLA composites. Interfacial adhesion and compatibility between PDLLA and bioactive ceramic

particles (HA and TCP) were investigated. Scanning electron microscopy (SEM) indicated that the interface between HA particles and PDLLA was blurred and HA particles were closely surrounded by PDLLA matrix in HA/PDLLA/MDI composites. Oriented fibrils along with longitudinal direction of extrusion die were also observed on the surfaces of HA/PDLLA/MDI composite. It is confirmed that MDI has improved interfacial adhesion and compatibility between HA particles and PDLLA phase. Fibril structures formed in the extrusion, and it contributed a great deal in enhancing the mechanical properties. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4085–4091, 2006

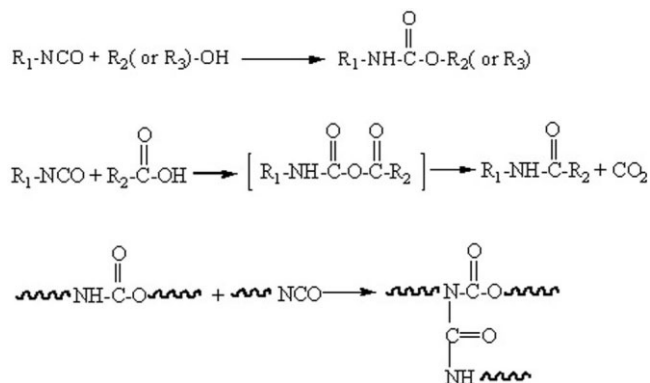
Key words: poly(D,L-lactide); bioactive ceramic particles; composites; mechanical properties; morphology

INTRODUCTION

Poly(lactide) (PLA) is a biodegradable aliphatic poly(lactone) esters with good biocompatibility. Its strength matches that of the bone during the process of bone healing and need not to be taken out by second surgeries. It is a promising material for bone plates and bone screw, and was authorized by FDA for using it in the refixation of bony fragments.^{1–5} However, PLA also has many disadvantages such as fast strength losing, poor toughness, and biological inertness. Therefore, studies on designing advanced processing method to improve PLA mechanical properties and combining with bioactive ceramic particles to improve bone-bonding ability of PLA attract many researchers.^{6–9} Recently, the composites of bioactive ceramic particles/PLA were prepared by physical mixing, such as solution mixing, melt mixing, and mechanical mixing. In these composite materials, interfacial adhesion and compatibility between PLA and bioactive ceramic particles is not well. To overcome these defects, Dupraz et al.¹⁰ have investigated the

effect of hydroxyapatite (HA) treated with silane coupling agents containing vinyl, methacryloxy, primary amine, secondary amine, and diamine functionality on the surface properties and ionic exchange of HA. The results showed that silane coupling agents were able to bond chemically on the HA surface and did not influence on the release of calcium and phosphate ions except aminosilane coatings. Quan et al.¹¹ also reported studies on the effect of surface modification of HA particles on the properties of HA/PDLLA composites. To increase the interfacial bonding between PDLLA matrix and HA particles, HA particles was treated with 3-trimethoxy-silylpropylmethacrylate (A-174). Their results showed that there are Si—O—P bonds on the surface of HA particles and the bending strength of HA/PDLLA composites greatly increased. Liu et al.¹² have proposed an *in situ* compatibilizing reaction to improve interfacial adhesion and compatibility between PDLLA and bioactive ceramic particles. By utilizing reaction of isocyanate group (—NCO) with active hydrogen, good compatibility was obtained in bioactive ceramic particles/PDLLA/MDI composites. In this paper, the author further investigated relationships between property and microstructure of bioactive ceramic particles/PDLLA/MDI composites prepared by the *in situ* compatibilizing reaction and piston extrusion.

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Scheme 1 Reaction mechanism of bioactive ceramic/PDLLA/MDI composites. R_1 refers to MDI, R_2 refers to PDLLA, and R_3 refers to HA.

EXPERIMENTAL

Materials

Lactic acid (analytical reagent; Guangzhou Chemicals Factory, China), stannous(II) octoate (chemical pure; Shanghai Chemicals, China), ethyl acetate (chemical pure; Guangzhou Chemicals Factory), methylenediphenyl diisocyanate (MDI, BASF chemical, Germany), anhydrous alcohol (chemical pure; Guangzhou Chemicals Factory), trichloromethane (chemical pure; Guangzhou Chemicals Factory), and anhydrous ether (chemical pure; Guangzhou Chemicals Factory) were used without further purification. Hydroxylapatite (HA) and tertiary calcium phosphate (TCP) were provided by Biomaterials Laboratory of College of Materials Science and Engineering in South China University of Technology.

Preparation of PDLLA

According to literature,^{13,14} PDLLA was synthesized by ring opening polymerization of *D,L*-lactide in the presence of stannous(II) octoate. At first, *D,L*-lactide was prepared using lactic acid in the presence of Sb_2O_3 and recrystallized three times from ethyl acetate before use. Second, refined *D,L*-lactide and stannous(II) octoate were sealed in dried glass ampoules under reduced pressure (<60 Pa) and immersed in an oil bath of $(135 \pm 5)^\circ\text{C}$ for 48 h. The products of polymerization were dissolved in trichloromethane and precipitated in anhydrous alcohol. The precipitate was filtered and washed by anhydrous alcohol, anhydrous ether in turn. The purified product (PDLLA) was dried under vacuum at 60°C to constant weight.

The molecular weight of PDLLA was measured by intrinsic viscosity and calculated by the following equation.¹⁴

$$[\eta] = 2.21 \times 10^{-4} M_v^{0.77}$$

where $[\eta]$ is the intrinsic viscosity and M_v is the viscosity average molecular weight. The intrinsic viscosity was measured by W's viscoscope. M_v of PDLLA prepared in this experiment is about 3.3×10^4 .

The molecular weight of PDLLA was also determined with respect to polystyrene standards by gel permeation chromatography (GPC). The results are M_n equals 1.4×10^4 , M_w equals 2.9×10^4 , M_z equals 4.6×10^4 , and polydispersity (M_w/M_n) is 2.04. The molar number of —OH group in PDLLA was calculated by M_n .

Thermal behavior of PDLLA was tested on TA Instrument DSC 2910 at a heating rate of $20^\circ\text{C}/\text{min}$ from 50°C to 200°C under nitrogen atmosphere. The result (Fig. 1) showed that its glass transition temperature (T_g) is about 47°C and melting temperature (T_m) is about 145°C .

Preparation of HA/PDLLA composite

The solution of PDLLA in trichloromethane and HA particles (15 wt%) were mixed. The mixture was precipitated in anhydrous alcohol. The precipitate was filtered and washed by anhydrous alcohol, anhydrous ether in turn. The purified product, called HA/PDLLA composite, was dried under vacuum at 60°C to constant weight.

Synthesis of bioactive ceramic/PDLLA/MDI composites

The solution of PDLLA in 1,4-dioxane, stannous(II) octoate, MDI, and HA or TCP particles were added into reaction vessels according to a designed ratio. The reaction vessel was immersed in an oil bath at $(95 \pm 2)^\circ\text{C}$ and the system was stirred under nitrogen atmosphere for 4 h. The product was precipitated in anhydrous alcohol. The precipitate was filtered and

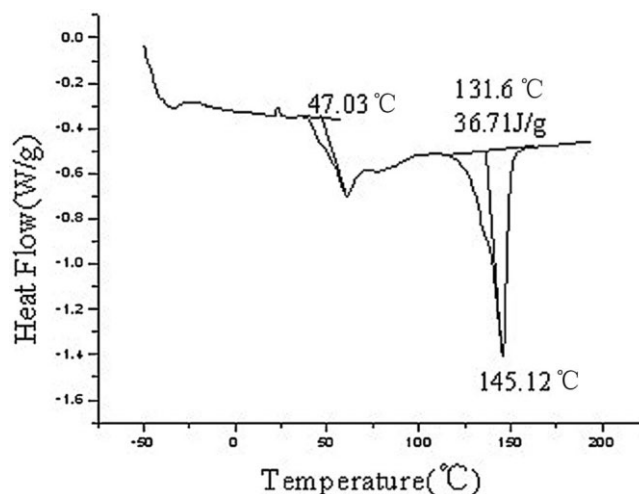


Figure 1 DSC analysis of PDLLA.

washed by anhydrous alcohol, anhydrous ether in turn. The purified products, HA/PDLLA/MDI and TCP/PDLLA/MDI composites, were dried under vacuum at 60°C to constant weight.

Preparation of bar samples of PDLLA and its composites

The bar samples with diameter 3.5 mm of PDLLA, MDI chain-extended PDLLA (PDLLA/MDI), and bioactive ceramic/PDLLA/MDI composites were obtained by piston extrusion at temperature between T_g and T_m . The bar was cut to length of 30 mm.

The measurement of bending strength and bending modulus of bars samples is carried out according to the method in literature.⁸ Samples were measured by three-point bending method on AG-I Universal Electronic Pulling Machine (Shimadzu, Japan) at room temperature and crosshead speed of 5 mm/min. Each data point was obtained from five samples. The maximum and minimum were omitted and the other three data were averaged.

Morphology

The bending fracture surfaces and longitudinal surfaces of these composites were observed by scanning electron microscopy (SEM) on a JEOL JSM-T300 instrument (Japan) after gold sputter. Some of the longitudinal split surface was etched by trichloromethane before gold sputter.

RESULTS AND DISCUSSION

Reaction mechanism of MDI chain-extending for bioactive ceramic/PDLLA/MDI composites

The isocyanate group ($-\text{NCO}$) is a very active functional group. It can react with active hydrogen such as $-\text{OH}$, $-\text{NH}_2$ or $-\text{COOH}$ group. PDLLA is a polymer that contains terminated $-\text{OH}$ and $-\text{COOH}$ group and the bioactive ceramic powder contains many $-\text{OH}$ groups too. Therefore, when MDI was added into mixture of bioactive ceramic powder and PDLLA, reactions as shown in Scheme 1 took place.

In the above reactions, the reaction of $-\text{NCO}$ group and $-\text{OH}$ group [eq. (1)] is a major reaction. The reactions between $-\text{NCO}$ group and $-\text{COOH}$ group [eq. (2)] and between $-\text{NCO}$ group and the amide hydrogen [eq. (3)] are side reactions. The reaction shown in eq. (1) was easily carried out at mild conditions, whereas that in eq. (2) and eq. (3) were carried out only under relatively stringent conditions such as high temperature, long reaction times or a lot of excess of $-\text{NCO}$ group.¹⁵ So, in the preparation of bioactive ceramic/PDLLA/MDI composites, $-\text{NCO}$ groups in MDI firstly reacted with $-\text{OH}$ groups in both PDLLA

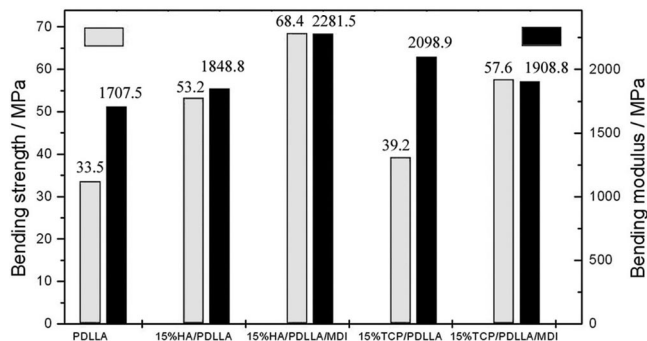


Figure 2 Bending strength and modulus of PDLLA and its composites at a processing temperature of 100°C.

and HA particles and formed chemical bonds between PDLLA and HA particles. However, in the HA/PDLLA composites prepared by solution mixing, there was only mechanical interlock between two phases and no chemical action. Therefore, interfacial adhesion in the HA particles/PDLLA/MDI composites is improved. As a result, the mechanical properties of HA particles/PDLLA/MDI composites were improved significantly.

Effect of MDI chain-extending on mechanical properties of HA/PDLLA/MDI and TCP/PDLLA/MDI composites

The mechanical properties of PDLLA, HA/PDLLA and TCP/PDLLA composites prepared by solution mixing and HA/PDLLA/MDI and TCP/PDLLA/MDI composites prepared by *in situ* compatibilizing reaction are given in Figure 2. The results showed that mechanical properties of bioactive ceramic/PDLLA composites prepared by different method have great difference at the same content of bioactive ceramic powder. The bending strength of HA/PDLLA and TCP/PDLLA composites is obviously bigger than that of PDLLA. After chain extending with MDI, its bending strength is nearly two times of that of PDLLA, which is 68.4 and 57.6 MPa, respectively. Comparing with that of HA/PDLLA and TCP/PDLLA composites, bending strength of HA/PDLLA/MDI and TCP/PDLLA/MDI composites has increased by 28% and 47%, respectively. Bending modulus of HA/PDLLA composites prepared by different method has the same tendency as the bending strength, but bending modulus of TCP/PDLLA composites basically has no difference. It is evident that adding MDI as chain-extender has improved the mechanical properties of these composites significantly.

Effect of MDI contents on mechanical properties of HA/PDLLA/MDI composites

To investigate the effect of content of MDI on the mechanical properties of HA/PDLLA/MDI compos-

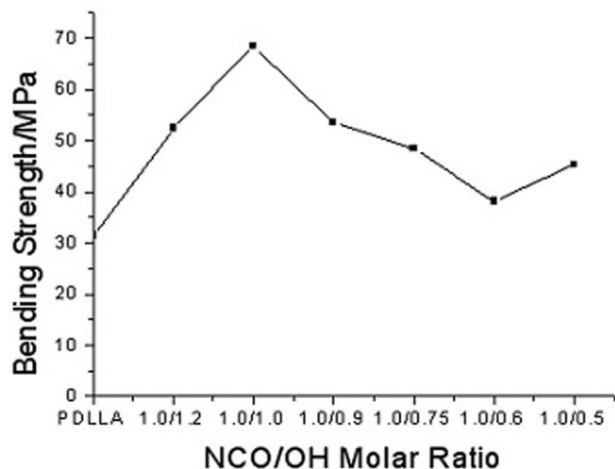


Figure 3 Effect of molar ratio of NCO/OH on bending strength of HA/PDLLA/MDI composites at a processing temperature of 100°C.

ites, these composites with different contents of MDI were synthesized at different molar ratio of —NCO groups in MDI to —OH groups in PDLLA and their mechanical properties were given in Figures 3 and 4.

Figures 3 and 4 showed that molar ratio of —NCO/—OH has obviously affected the bending strength and bending modulus of HA/PDLLA/MDI composites. When molar ratio is 1.0/1.0, the mechanical properties of HA/PDLLA/MDI composite containing 15 wt % HA reach maximum, with the bending strength of 68.4 MPa and bending modulus of 2281.5 MPa. According to the mechanism mentioned earlier, the optimum mechanical properties of HA/PDLLA/MDI composites should be occurred at molar ratio of 1.0/1.0. When molar ratio of —NCO/—OH is higher than 1.0/1.0, with increasing molar ratio of —NCO/—OH, the bending strength of HA/PDLLA/MDI composites has decreased and its bending modulus almost unchanged, but when molar ratio of —NCO/—OH increased to 1.0/0.5, its bending modulus decreased rapidly. However, when molar ratio of —NCO/—OH was lower than 1.0/1.0, both bending strength and bending modulus of this composite have increased with increasing molar ratio of —NCO/—OH. The authors believed that when the molar ratio of —NCO/—OH is more than 1.0/1.0, the amount of —NCO groups was remnant and these remnant —NCO groups continue to react with —COOH groups in PDLLA and urethane groups and form branched structure, but at the molar ratio of —NCO/—OH less than 1.0/1.0, the amount of —NCO groups was not enough to make sufficiently linkage between PDLLA molecular chains and HA powder. Therefore, the effect of compatibility between PDLLA and HA was improved with increasing amount of MDI.

Effect of processing conditions on the mechanical properties of HA/PDLLA/MDI composites

The preparation of bar samples of PDLLA and its composites in our experiments was divided into two steps: first, compression molding to form a pillar with diameter of 14 mm, then piston extruding to prepare a bar of diameter 3.5 mm. Liu et al.¹² has systemically investigated the influence of compression-molding conditions and extrusion conditions on the mechanical properties of PDLLA and HA/PDLLA composites and concluded that processing condition is one of the important factors that affect the mechanical properties of PDLLA and HA/PDLLA composites. In this paper the effect of processing conditions on the mechanical properties of HA/PDLLA/MDI composite was further investigated. The experimental results of effect of compression-molding conditions on the mechanical properties of PDLLA and HA/PDLLA/MDI composites were given in Table I.

The results in Table I showed that compression-molding temperature and conditioning time have great influence on mechanical properties of HA/PDLLA/MDI composites. When the compression-molding temperature increases from 100 to 165°C, the bending strength of PDLLA is increased by only 5%, but its bending modulus is increased by about 40%. However, the results of 15%HA/PDLLA/MDI composites are opposite. With the increasing compression-molding temperature or increasing Conditioning time, bending strength of HA/PDLLA/MDI composites decreased rapidly. When conditioning temperature increased from 100 to 120°C, its bending strength decreased 16.5% only, whereas from 120 to 140°C, the bending strength decreased about 57%, even if at 120°C, when conditioning time postponed from 30 to 60 min, the bending strength almost decreased about

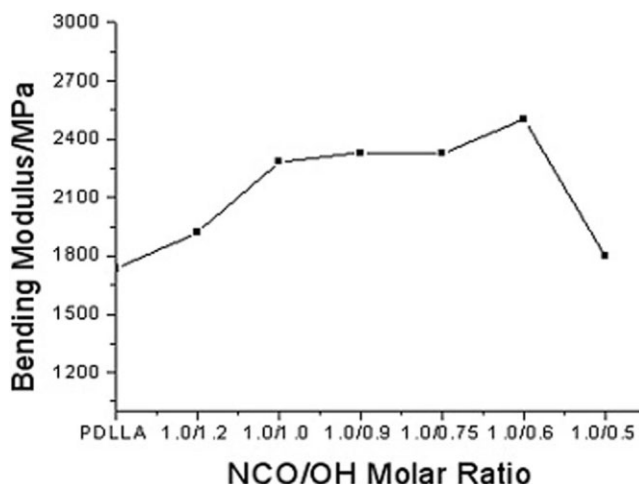


Figure 4 Effect of molar ratio of NCO/OH on bending modulus of HA/PDLLA/MDI composites at processing temperature of 100°C.

TABLE I
Effect of Compression Molding Conditions on the Mechanical Properties of PDLLA and 15% HA/PDLLA/MDI Composites

Compression molding conditions		Bending strength (MPa)		Bending modulus (MPa)	
Temperature (°C)	Conditioning time (min)	PDLLA	HA/PDLLA/MDI	PDLLA	HA/PDLLA/MDI
100	30	33.5	54	1707.5	2215.3
120	30	34.7	45.1	1846	2392.5
120	60	–	19.8	–	2139.3
140	30	–	19.2	–	1970.8
165	30	35.1	8.1	2413.6	1806.7

Extrusion conditions: temperature, 100°C; conditioning time, 30 min.

56%. The effect of compression-molding conditions on its bending modulus is the same as that of the bending strength. After bending modulus of HA/PDLLA/MDI composites got maximum at compression-molding temperature 120°C and conditioning time 30 min, its bending modulus rapidly decreases with increasing compression-molding temperature. It is evident that MDI chain extending obviously reduced thermal stability of HA/PDLLA/MDI composites. This is because the urethane structure in the composites has poor thermal stability and was easily degraded at over 120°C.

To avoid degradation of HA/PDLLA/MDI composites, 100°C was selected as extruding temperature and the effect of conditioning time at this temperature on its mechanical properties was investigated. The experimental results were given in Table II.

The results in Table II showed that conditioning time at extruding process also affected mechanical properties of HA/PDLLA/MDI composites. With increasing conditioning time, both bending strength and bending modulus have increased. When conditioning time is over 45 min, its mechanical properties did not increase obviously. The optimum conditioning time is about 45 min.

Morphology of HA/PDLLA/MDI composites

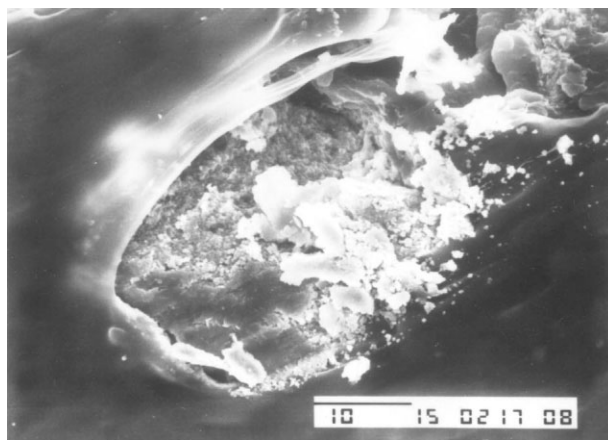
SEM results on bending fracture surfaces of HA/PDLLA and HA/PDLLA/MDI composites were shown in Figure 5.

TABLE II
Effect of Extrusion Conditions on the Mechanical Properties of HA/PDLLA/MDI Composites

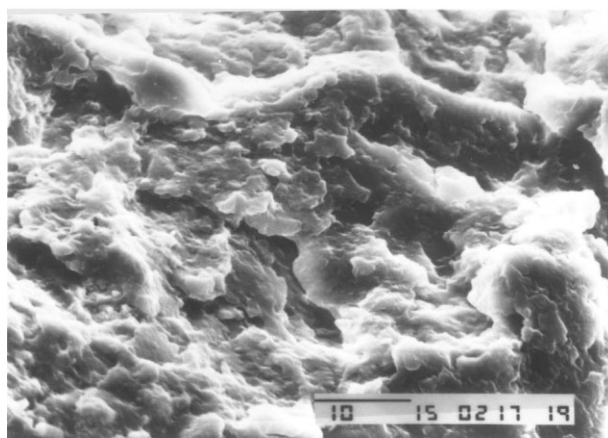
Extrusion conditions		Bending strength (MPa)	Bending modulus (MPa)
Temperature (°C)	Conditioning time (min)		
100	30	38.1	1878.4
100	45	41	1946.3
100	60	41.9	1983.1

Compression-molding conditions: temperature, 100°C; conditioning time, 30 min.

Figure 5 revealed that morphology of bending fracture surfaces of HA/PDLLA and HA/PDLLA/MDI composites have great difference. In HA/PDLLA composite prepared by solution mixing, HA particles gathered together inside PDLLA matrix and interface between HA particles and PDLLA was very clear in Figure 5(a). But in HA/PDLLA/MDI composite pre-



(a)



(b)

Figure 5 SEM micrographs of bending fracture surfaces of PDLLA composites: (a) HA/PDLLA composite (×1000), (b) HA/PDLLA/MDI composite (×1000).

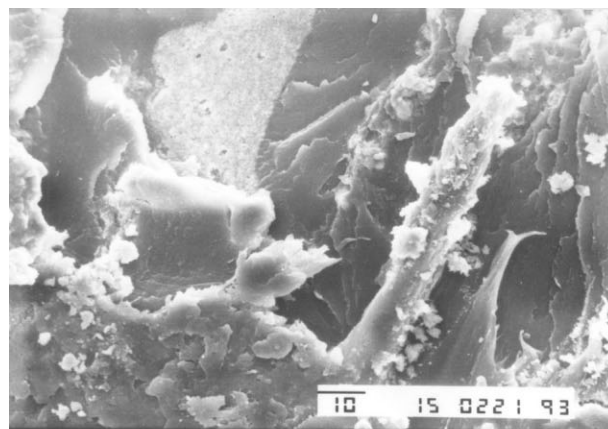
pared by *in situ* compatibilizing reaction, HA particles were tightly bonded by PDLLA matrix and can hardly be observed from the fracture surface. The interface between HA particles and PDLLA was blurred in Figure 5(b). It is confirmed that interfacial cohesive force and compatibility between HA particles and PDLLA matrix were improved obviously by adding MDI as chain-extender. In fact, MDI chain-extender in HA/PDLLA/MDI composites has played a role of coupling agent and formed chemical bond between HA particles and PDLLA matrix. Therefore the mechanical properties of HA/PDLLA/MDI composites were better than that of HA/PDLLA composite.

Figure 6 is morphology of longitudinal split surface of HA/PDLLA composite and HA/PDLLA/MDI composite. The results showed that on their longitudinal split surface there are fibril structures that are oriented along with longitudinal axis, and these fibril structures were more clearly observed from etched surface in Figure 6(c).

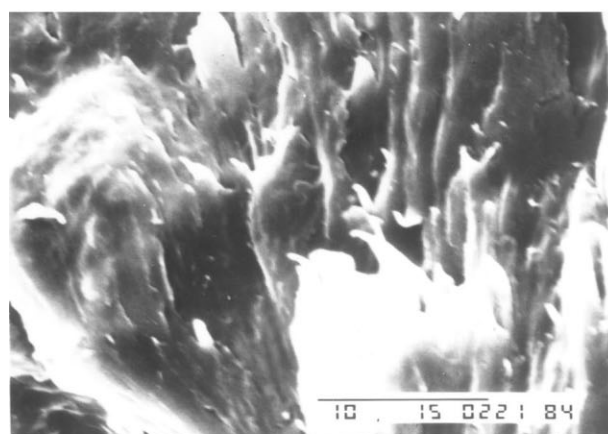
The formation of fibril structure is attributed to the extruding process. When HA/PDLLA composite and HA/PDLLA/MDI composite were extruded from compression-extruding equipment at temperature between T_g and T_m , molecular chains of polymer were forced to orient along with longitudinal axis. This fibril structure has a great contribution in enhancing mechanical properties of these composites. However, longitudinal split surface of HA/PDLLA composite is significantly different from that of HA/PDLLA/MDI composite. In the surface of HA/PDLLA composite [shown in Fig. 6(a)], many particles separate from PDLLA matrix, whereas in the surface of HA/PDLLA/MDI composite [shown in Fig. 6(b)], the particles were hardly observable. Even if on the etched longitudinal split surface [shown in Fig. 6(c)], some particles observed were blurred by PDLLA. This result is also proved that MDI as chain extender has improved the interfacial compatibility of the composites.

CONCLUSIONS

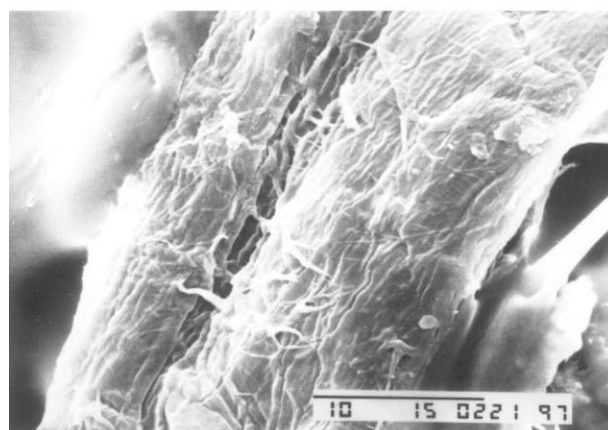
Composites of bioactive ceramic particles/PDLLA/MDI were prepared by *in situ* compatibilizing reaction using MDI as chain-extender and reactive compatibilizer. Their mechanical properties increased obviously and interface cohesive force and compatibility of PDLLA with HA and TCP got improved. The content of MDI have great influence on their mechanical properties. At the optimum conditions of 1.0/1.0 molar ratio of $-NCO$ groups in MDI to $-OH$ groups in PDLLA, 15 wt % HA/PDLLA/MDI composite with the best bending strength 68.4 MPa and bending modulus 2281.5 MPa was prepared. Both increased by nearly 30% when compared with that of HA/PDLLA composites.



(a)



(b)



(c)

Figure 6 SEM micrographs of surface of HA/PDLLA and HA/PDLLA/MDI composites: (a) longitudinal split surface of HA/PDLLA composites ($\times 500$), (b) longitudinal split surface of HA/PDLLA/MDI composite ($\times 1750$), (c) longitudinal split surface etched by trichloromethane of HA/PDLLA/MDI composite ($\times 1750$).

Processing conditions affected the mechanical properties and microstructure of PDLLA and bioactive ceramic particles/PDLLA/MDI composites. With in-

creasing compression molding temperature, mechanical properties of PDLLA increased slightly, but for composite of 15 wt % HA/PDLLA/MDI, the strength decreased rapidly at over 120°C. In the process of compression extrusion molding, molecular chains of HA/PDLLA/MDI composites are forced to orient along with longitudinal axis and form fibril structure. This fibril structure has a great contribution in enhancing their mechanical properties.

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