

# Preparation and Degradation of PLA/Chitosan Composite Materials

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**ABSTRACT:** As scaffold material, poly(lactic acid) (PLA) has several obvious weaknesses, such as fast biodegradation, acidic degradation product, and hydrophobicity. To solve these problems, a series of PLA/chitosan composite materials was prepared in this study. SEC observation, porosity tests and contact angle measurements showed that the materials were hydrophilic and had appropriate porosity and structure, which were favorable to the cell growth.

Degrading tests *in vitro* indicated that the degrading speeds of the materials were slower than that of PLA, and the materials could keep adjacently litmusless, certain shape and mechanical properties. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 274–277, 2004

**Key Word:** degradation; composites; hydrophilic polymers

## INTRODUCTION

Poly(lactic acid) (PLA) is biocompatible and undergoes scission in the body to monomeric units of lactic acid, which is a natural intermediate in carbohydrate metabolism. These characteristics make this polymer suitable for use in resorbable sutures, as a carrier for the controlled release of drugs, and as implants for orthopaedic surgery or blood vessels, which will eventually be replaced by the body's tissue.<sup>1</sup>

However, as a scaffold materials, PLA has several obvious weaknesses, such as past biodegradation, acidic degradation product, and hydrophobicity. When PLA is planted in the body, the degradation takes place synchronously. It is slow at first, and the low molecular weight acidic product is discharged by metabolism. As the reaction speeds up, the acid hasn't enough time to be removed and accumulates, which will accelerate the degradation. It is thought that many nonbacterial inflammations are aroused by the acidic product.<sup>2</sup> To solve these problems, a series of PLA/chitosan composite materials was prepared in this study. Chitosan is another biocompatible and biodegradable materials, which is used widely in biomedical applications like surgical sutures and devices for internal bone fixation.<sup>3</sup> It is hydrophilic as well. There are many -OH and -NH groups in chitosan, which cause strong intramolecular and intermolecular hydrogen bonds; thus the infiltration and diffusion of

water is restrained. What's most important is that chitosan is a rare alkaline polysaccharide in nature. Its alkalescence can effectively neutralize the acidic product of PLA, so the PLA/chitosan composite material will be a more biocompatible bioscaffold. The effects of chitosan on the biodegradation of PLA was studied in this article, and the biological evaluations of the composites will be undertaken in a future article.

## EXPERIMENTAL

### Materials

PDLLA was purchased from the Medical Apparatus Institute of Shandong, China. Chitosan, with a degree of deacetylation of more than 90%, was supplied by BOAO Biotechnic Cooperation of Shanghai.

### Preparation of PLA/chitosan composite materials

PLA, 10:1 (w/w) chitosan (diameter 0.054 mm) and NaCl (diameter 120  $\mu\text{m}$ ) were mixed with agitation under vacuum at 160°C for 30 min. Then the mixture was placed on a clear, sterile, coarse Teflon plate and molded. The composite material was dipped in distilled water to exude NaCl grain, and then it was dried.

The weight proportions of PLA to chitosan in the composite materials ranged from 10 : 1 to 10 : 4.

### SEM observation of materials

The materials were dehydrated under vacuum and then gilded. The surfaces of the samples were evaluated with a JAPAN HITACHI S-520s scanning electron microscope.

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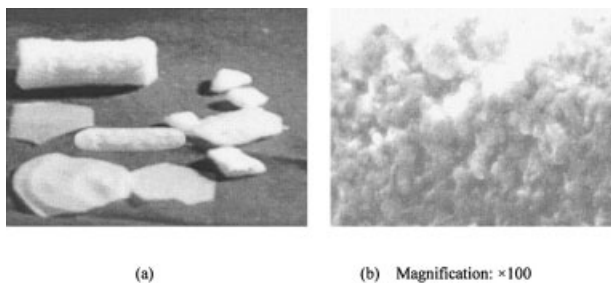


Figure 1 Configuration of composite materials.

**Contact angle measurement**

A series of PLA/chitosan composite membranes was prepared according to the above method, but the surfaces were slick. The contact angles were measured with a CAM-PLUS Contact Angle Meter.

**Porosity test<sup>4</sup>**

Into a pycnometer of ethanol of weight  $W_1$  was dipped a sample (weight  $W_s$ ). When the cavities of the material were full of ethanol, measured amount of ethanol was added to fill the pycnometer, of which the gross weight was  $W_2$ . The sample was taken out, and the remainder weighted  $W_3$ .

According to the calculator formula for porosity  $\epsilon = (W_2 - W_3 - W_s) / (W_1 - W_3)$

**Degradation *in vitro***

PLA/chitosan composite materials were weighted precisely and then put into 10 mL of normal saline, sealed and shaken at 37°C. Extractions of the samples were tested with PHS-3S PH Meter, and the normal saline was changed each week. The materials were then cleaned, dehydrated and weighted to calculate the weight loss rate (WLR):

$$WLR: dw = (W_0 - W) / W_0 \times 100\%$$

$W_0$  and  $W$  refer to the initial weight a week before and the surplus weight after one-week of degrading respectively.

**RESULT AND DISCUSSION**

**Preparation**

PLA/chitosan lacunaris composite materials are light yellow and can be molded into different shapes, such as membrane, fluke, tube, etc, as shown in Figure 1(a).

The surfaces of materials used as tissue engineering scaffolds are required to be coarse and to have appropriate porosity and structure, which favor cell growth. Therefore the composite materials were molded on a

coarse Teflon plate. Figure 1(b) shows the configuration of the materials.

**SEM observation of materials**

Figure 2 indicates that the diameters of the pores were more than 100  $\mu\text{m}$  and that the pores, including the inner ones, were connected. Tissue engineering research has found that scaffold materials must possess three dimensional lacunaris structures, and that the pores must be more than 100  $\mu\text{m}$  in size. Thus the micropole structure will allow the cells larger contact surface, and will be favorable for cell adherence, exchange of nutrition with surroundings, and discharge of waste.

**Porosity test**

The classic method to test the porosity of materials uses hydrargyrum, but this chemical is poisonous and volatile, so the pycnometer method was applied in this test, which is easy to control and repeat. The porosity can be calculated by the following formulas:

$$\text{Sample volume: } V_s = (W_1 - W_2 + W_s) / \rho$$

$$\text{Pore volume: } V_p$$

$$= (W_2 - W_3 - W_s) / \rho$$

$$\text{Porosity: } \epsilon$$

$$= (W_2 - W_3 - W_s) / (W_1 - W_3)$$

Table I shows the influence of NaCl weight fraction on the porosity of the scaffolds. It clearly indicates that the porosity increases with the increasing fraction of NaCl in the composite materials. That is to say the separation of NaCl created the pores, so the porosity can be controlled by controlling the weight fraction of NaCl.

Shown in Figure 2, SEM observation also indicates that the composite materials possessed lacunaris net structures. The larger the NaCl grain, the bigger the diameter. Controlling the NaCl grain size can control the diameter of the pores. In the test, 40~60% NaCl

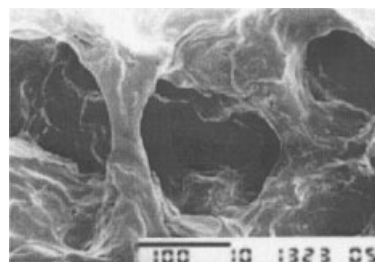


Figure 2 SEC observation of materials (magnification  $\times 2000$ ).

**TABLE I**  
Relationship Between NaCl Weight Fraction in Composite Materials and Porosity of Scaffolds

Sample	NaCl Weight Fraction	Porosity
1	59.5%	58.3%
2	66.5%	63.1%
3	75.3%	74.0%
4	85.3%	84.3%
5	91.1%	89.2%
6	92.0%	91.2%

grains were selected, and their weight fraction in the composite materials was over 90%.

### Contact angle measurement

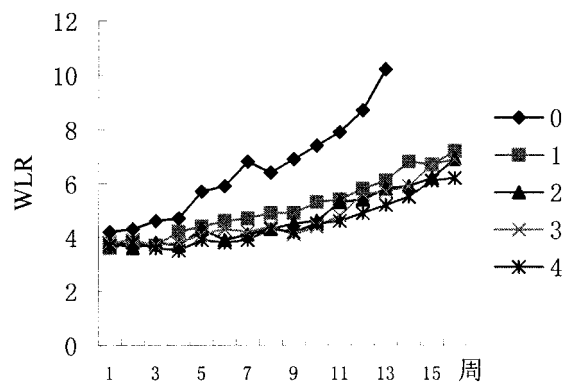
Contact angle measurements of liquid droplets on substrate surfaces are used to characterize surface wettability, surface cleanliness and the hydrophilic/phobic nature of the surface. The contact angle is defined as the angle between the substrate support surface and the tangent line at the point of contact of the liquid droplet with the substrate. A liquid drop is placed on a solid substrate, and the contact angle has a single value for smooth, homogeneous substrate surfaces. The value of the contact angle of the liquid droplet will depend on the surface energy of the substrate and the surface tension of the liquid. If complete wetting takes place between the liquid and the substrate surface, the droplet will spread out over the substrate and the contact angle will approach zero, whereas if wetting is only partial, the resulting contact angle will lie in the range of 0–180°

Composite material surfaces may not be completely homogenous, so the surface energies are not evenly distributed; therefore, the measurement of contact angles on solid surfaces were taken at 10 points on the tested surface. PLA/chitosan composite membranes without NaCl were used in the tests.

Table II shows the effect of chitosan on the contact angles of the composite materials. Obviously, the general trend is that the contact angles decrease with the increased weight fraction of chitosan; that is to say, the addition of chitosan is beneficial to improving the hydrophilicity of the materials. Chitosan is more hydrophilic than PLA, so it can improve the biocompatibility of the composite materials as scaffolds.

**TABLE II**  
Contact Angles of PLA/Chitosan Composite Membranes

Sample	PLA	PLA/Chitosan Ratio			
		1:0.1	1:0.2	1:0.3	1:0.4
Contact angle (°)	78	70	63	58	54



**Figure 3** Weight loss rate (WLR) curves of the composite materials during the degradation.

### Degradation test *in vitro*

Three samples were used from each group during the degrading test. The test was carried out over 16 weeks, because the PLA materials were already fragmented after 14 weeks and the pieces could be removed from the body.

When PLA is planted in the body, the degradation takes place synchronously. It is slow at first, and the low molecular weight acidic product can be discharged by metabolism. As the reaction speeds up, the acid hasn't enough time to be removed and accumulates which accelerates the degradation, a process called self-catalysis.<sup>6</sup> Degradation occurs the same way during the test *in vitro*, so the WLR of the PLA was nearly constant for the first 4 weeks, and it increased noticeably later, as shown in Figure 2. The contacting interface got larger, producing many holes inside, which also accelerated the degrading speed.

In Figure 3, the numbers from 0 to 4 refer to pure PLA and 1:0.1 to 1:0.4 (wt/wt) PLA/chitosan composite materials, respectively.

According to Figure 3, the WLR increased with the increase of degradation time, but the WLR of the composite materials changed slowly compared to that of the pure PLA. And with the increase of the chitosan weight fraction in the composite materials, the WLR decreased within the same time span. This is because chitosan is alkaline, and it can neutralize the acidic product of the PLA, so the self-catalysis is restrained to some degree.

The PH of the solutions was studied each week. The degradation test took place over a long time, and the ambient temperature changed much, so the test, including measuring, was conducted in 37°C water bath.

The PH meter was adjusted with a potassium acid phthalate buffer solution and a phosphoric acid buffer solution (PBS) before each measurement.

The average PH of the normal saline was 6.93 under the same conditions.

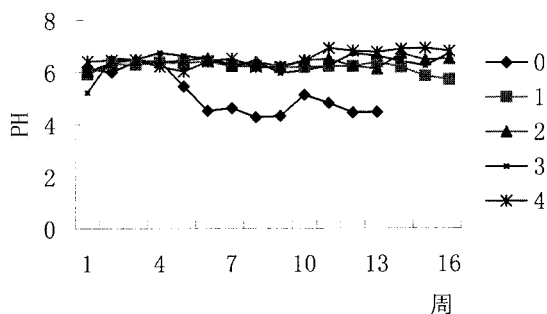


Figure 4 PH of the composite materials during the degradation.

Figure 4 shows the effect of chitosan on the PH of the solution during degradation.

Figure 4 indicates that the PH of the PLA solution stayed at 6.0 during the first 4 weeks, but it decreased quickly later and changed near 4.5. However, the pH values of the PLA/chitosan composite materials were always at 6.40. What's more, with the increased weight fraction of chitosan, the pH got higher, especially the pH of the 1:0.4 composite material, which was very close to that of the normal saline. The alkalinity of the chitosan was also used to explain this phenomenon. However, the PLA weight fraction of the composite materials decreased during the last

weeks, so the acidity of the extraction decreased, which made the PH increase slightly.

The other significant thing is that the composite materials could keep their initial shapes and certain mechanical properties, but the pure PLA materials became curved and friable during the test. That is to say, the composite materials possess more useful properties as scaffolds than PLA, which conforms to our expectations.

## CONCLUSIONS

From the above, we can see that the PLA/chitosan composite materials are hydrophilic and possess the suitable three-dimensional lacunaris, cavity ratio and diameter. Degradation tests *in vitro*, indicates the degrading speeds of the materials are slower than that of PLA, and the materials could keep adjacently litmusless, certain shape and mechanic property.

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