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ORIGINAL PAPER

In vitro degradation behaviors of Poly-L-lactide/bioactive glass composite materials in phosphate-buffered solution

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Abstract In vitro degradation behaviors of composite materials composed of poly-L-lactide (PLLA) and bioactive glass (BG) were systematically investigated up to 20 weeks in phosphate-buffered solution (PBS) at 37 °C. The properties of PLLA/BG composites and PLLA materials, including weight loss, bending strength and modulus, shearing strength, polymer molecular weight and its distribution, and the morphologies, were investigated as a function of degradation time. The change of the pH value of the PBS media was also detected. The results showed that the presence of the bioactive glass modified the degradation of the matrix polymer. The degradation rate of the PLLA/BG composites was slower than the degradation rate of the sole PLLA materials.

Keywords Poly-L-lactide · Bioactive glass · Composite materials · Degradation behaviors · In vitro

Introduction

Poly-L-lactide (PLLA) as a polymer material has been applied to a variety of biomedical products such as degradable sutures, temporary orthopedic fixtures and tissue engineering scaffolding materials [1–3], for the following reasons-producible from renewable resources, very low or nontoxic in natural environments, biodegradable, and compostable. Moreover, PLLA has a higher mechanical

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performance compared with that of commercial polymers such as polyethylene, polypropylene, and polystyrene.

The degradation of PLLA has been extensively studied under different conditions in vitro and in vivo [4, 5]. The degradation mechanism is mainly hydrolysis, which is affected by many factors such as chemical structure, molecular weight, device morphology, size and geometry, processing method, impurities, additives, in vitro or in vivo environment [6, 7]. Due to the various factors which affect the degradation and thus to the relatively complex degradation mechanism, exact prediction of degradation behavior is difficult.

Recently, increasing attention has been paid to fabricatecomposite biomaterials [8, 9]. The implants made of these materials offer a combination of several functions. Osteoconductive calcium phosphates, such as hydroxyapatite and β-tricalcium phosphate, have also been used successfully to improve the biocompatibility and osteoconductivity of bioabsorbable polymers [10–12].

An understanding of the effect of the added compounds on matrix degradation is essential. Several studies have been carried out on the degradation of PLLA and calcium phosphates [13, 14] as such. Some properties of the different material combinations can be estimated based on these earlier studies, but usually the degradation behavior is the characteristic for each filler/matrix material combination making prediction complicated. It depends on various factors, such as microstructural, macrostructural and environmental factors. Therefore it is essential to determine the effect of the added compounds on the degradation behavior of the material. In this paper, the degradation behaviors of poly-L-lactide and its bioactive glass containing composite in vitro were investigated.

Experimental

Materials and manufacturing the composites

The raw materials used in this study were high weight average molecular mass poly-L-lactide (8.75×10^5 Da) and bioactive glass with a composition of 35CaO, $60SiO_2$, $5P_2O_5$ (mol.%). Poly-L-lactide was obtained through ring-opening polymerization [15]. Bioactive glass with a mean particle size 4.24 μm was prepared by sol–gel method according to the previous reference [16]. Briefly, sol was prepared from teraethylortosilicate (TEOS), deionized water as solvent, hydrochloric acid as catalyst, and calcium nitrate and triethyl phosphate (TEP) as CaO and P_2O_5 precursors, using a molar ratio of HCl and H_2O to TEOS and TEP of 8. The synthesis was made at a low pH causing a spontaneous gelation owing to hydrolysis of TEOS and subsequent condensation of formed Si–OH groups. The sol was kept 3 days at room temperature to allow the hydrolysis and polycondensation reaction until the gel was formed. For aging, the gel was heated at 60 °C for 3 days. The dried gel was heated at 160 °C for 2 days, then was ground for 8 h. Bioactive glass particle size and size distribution of the resulting powder were analyzed by Laser Scattering Particle Size Distribution Analyzer (Microplus).

The polymer was compounded with bioactive glass in weight proportion 90/10 at 185 °C. Briefly, the polymer was dissolved in CH_2Cl_2 to produce a polymer weight to solvent volume ratio of 5% (w/v). The mixture was stirred overnight to obtain a homogeneous polymer solution. Bioactive glass powder with a content of 10 wt% was added into the polymer solution. The mixture was transferred into a flask and sonicated for 60 min in order to improve the dispersion of the bioactive glass particles into the polymer solution. After homogenization, the mixture was cast onto a flat glass plate to obtain flake then dried in a vacuum drying oven at 40 °C. Rectangular bars with effective dimensions of 37.5 mm × 6.3 mm × 3.5 mm for bending and shearing was compressed under 110 MPa at 185 °C and subsequently annealed at 115 °C for 20 min and naturally cooled to room temperature.

In vitro hydrolysis

The hydrolysis of the PLLA and PLLA/BG composites were performed in a glass bottle with 30 ml phosphate-buffered solution (pH = 7.4) at 37 °C. The degradation system was kept dynamic and was sampled monthly (The samples were taken out of the degradation medium and washed with de-ionized water). They were then dried in vacuum at 40 °C for further testing and characterization.

Characterization of the samples

The water uptake and weight loss of the PLLA and PLLA/BG composites were evaluated in a 7.4 pH PBS at 37 °C. The samples, before degradation, were dried in vacuum and the weight was measured in an analytical balance. The samples, during degradation, were first taken out of the degradation medium at different times. The water uptake of PLLA and PLLA/BG samples was calculated by comparing the weight difference of the wet and the dried sample. The samples were washed with de-ionized water and then dried in vacuum to eliminate all the residual medium liquids. These weights were then compared with the original sample weights before the degradation to calculate the percentage weight loss during the specific degradation time according to the following equation [17]:

$$W_l\% = 100 \times (W_d - W_0)/W_0 \quad (1)$$

$$W_u\% = 100 \times (W_s - W_d)/W_d \quad (2)$$

where W_l, W_u, W_s, W_d, and W_0 is the weight loss, water uptake, wet weight, dried weight, and initial weight of PLLA and PLLA/BG sample, respectively. Five samples from every group were used for the water uptake and weight loss tests.

In order to evaluate the molecular weight and molecular weight distribution changes of PLLA, gel permeation chromatography (GPC) was performed on Waters 510, and the data processing software was Waters Millennium 32. The equipment consisted of a differential refractometer detector (Waters 410 RI), Shodex KF-800 columns and HPLC-pump (Waters 515). Samples were measured at 35 °C with chloroform as eluent at a flow rate of 1.0 mL min^{-1}. The molecular weight was calibrated relative to polystyrene standards.

To evaluate the initial mechanical properties of the samples, the dried samples were mechanically tested at room temperature by three-point bending and shearing using mechanical testing apparatus (Instron 1121, UK). Bending strength, bending modulus and shear strength were measured in vitro under dry conditions at room temperature. All the given values are mean values of five measurements (±standard deviation).

The surface and fracture morphologies of the initial and cultivated samples at different degradation stages were studied with KYKY-2800 scanning electron microscopy (SEM). The samples were first dried and sputter-coated with gold in vacuum.

Results and discussion

The changes of pH value of phosphate-buffered solution

The changes of the pH value of PBS with PLLA and PLLA/BG samples are shown in Fig. 1. For PLLA samples, during the first week of degradation, the pH value of PBS changed relatively little, after 1 week of degradation, the pH value dropped slightly and then followed a quick decrease (4.0–4.5) after 6 weeks. After 12 weeks the pH value kept relatively unchanged (pH 3.0). For PLLA/BG materials, the pH of the buffer solution remained constant (pH 7.4) for up to 6 weeks in vitro, and then decreased slightly, However, the pH value always keeps a higher level (around 7.0). It can be assumed that the hydrolysis of bioactive glass creates the hydroxyl ions into the surrounding buffer solution. The hydroxyl ions can bind hydrogen ions from the solution and thus act as an alkali. This is thought to neutralize the acidic

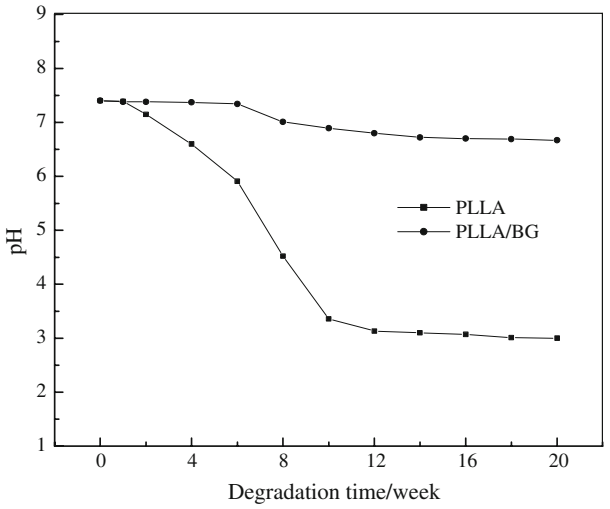

Fig. 1 pH change of PBS with degradation time

degradation products of PLLA, thus stabilizing the pH of the buffer solution. Neutralizing and stabilizing effects have been reported for other composites [12].

Weight loss of the samples

The weight of the PLLA/BG and PLLA sample were measured throughout the degradation period as shown in Fig. 2. The weight loss of both samples increased with time, which was caused by the hydrolysis of PLLA and the shift of bioactive glass. The weight loss of PLLA sample was higher than that of PLLA/BG sample. The results showed that the bioactive glass addition reduced the overall degradation rate in terms of mass loss. After water gets into the polymer matrix, it hydrolyzes the amorphous areas and leaves the crystalline parts to be dropped off from the matrix, and leads to an increase in the mass loss. This is proven by the experimental observation that after hydrolysis for 8 weeks, many insoluble, small grains were observed to suspend in the degradation medium when shaking the glass bottle containing the sample. As the degradation time increased, water molecules continue to enter into the polymer matrix and hydrolyze the crystalline areas of the PLLA matrix.

Water uptake of the samples

The water uptake of PLLA and PLLA/BG samples are presented in Fig. 3. Water absorption increased dramatically before 8 weeks, and then followed a slight increase. This indicates that water absorption has reached saturation after 12 weeks. The water uptake was higher in the composites than in PLLA materials, which is probably due to the interfaces between the bioactive glass particles and matrix polymer of the composites.

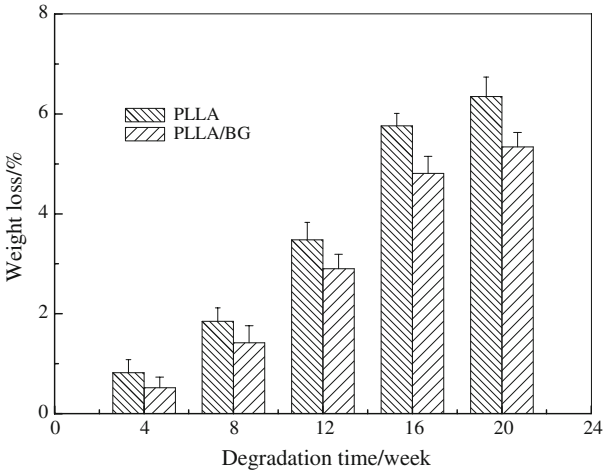

Fig. 2 Weight loss of PLLA and PLLA/BG during degradation in phosphate-buffered solution

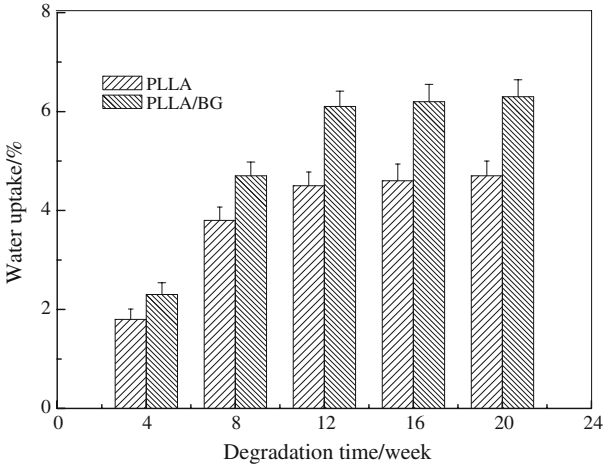

Fig. 3 Water uptake of PLLA and PLLA/BG during degradation in PBS solution

Changes of molecular weight and GPC curves

Figure 4 shows the GPC results of the PLLA and PLLA/BG samples after different time of hydrolysis degradation. It can be seen that as degradation continued, retention time of all the samples slowly shifted to the right, which means the molecular weight decreased. In addition, after 20 weeks of degradation, the molecular weight distribution curves of PLLA and PLLA/BG samples became broader; however, the molecular weight distribution of PLLA materials was slightly broader than that of PLLA/BG composite materials.

Table 1 shows the changes in molecular weights (M_n and M_w) of the PLLA and PLLA/BG materials with the degradation time. It is obvious that the molecular weight decreased continuously with an increase in the degradation time. After 20 weeks of degradation, the molecular weight loss of the PLLA materials was larger than that of the PLLA/BG composites. The weight average molecular mass loss of PLLA in each of the samples is 45.6% and 35.8%, respectively, indicating that the polymer in the PLLA materials is degraded slightly faster than those in the PLLA/BG composites. The reason may be that the carboxyl groups produced by the hydrolysis of PLLA accelerates its degradation; while, the hydroxyl ion produced by hydrolysis in the PLLA/BG composites neutralized the acidic degradation products and thus inhibited the degradation of PLLA. Comparing Table 1 with Fig. 2, it is obvious that the changes in the molecular weights and the masses are not synchronous. This can be understood because the breakage of the ester bonds during degradation leads to the formation of low molecular weight products, and thus molecular weight decreases continuously and the molecular weight distribution becomes increasingly broader. On the other hand, during degradation only a small portion of the degraded macromolecular fragments will become small enough to be soluble in the phosphate-buffered solution, and therefore the mass losses lag behind the molecular weight decreases [18].

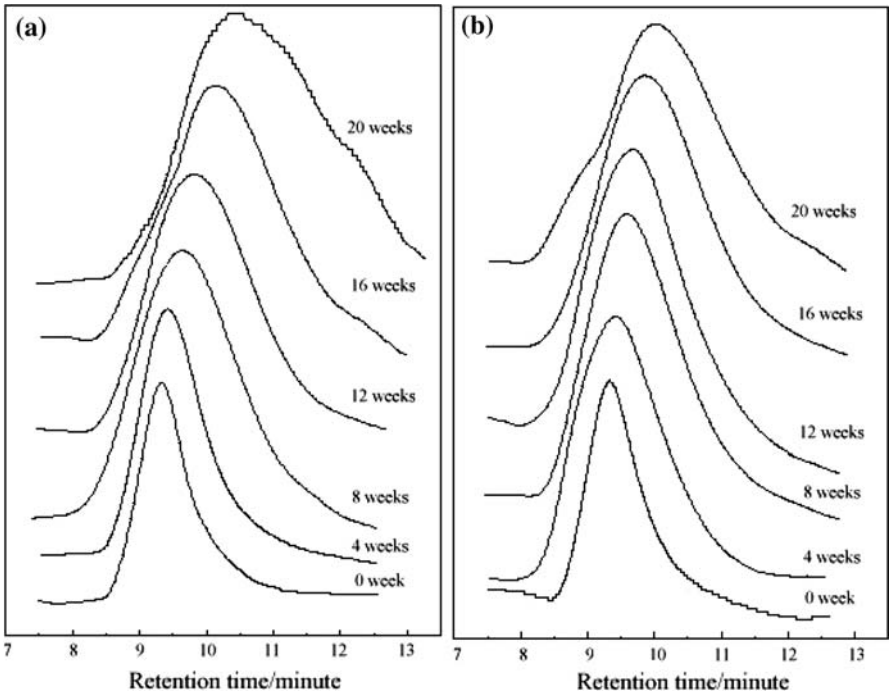

Fig. 4 GPC of PLLA and PLLA/BG materials with degradation time: **a** PLLA; **b** PLLA/BG

Table 1 Changes of molecular weight and polydispersity index of PLLA and PLLA/BG composite with degradation time

Degradation time/week	Number average molecular mass/$\times 10^5$ Da		Weight average molecular mass/$\times 10^5$ Da		Polydispersity index	
	PLLA	PLLA/BG	PLLA	PLLA/BG	PLLA	PLLA/BG
0	7.459	6.954	8.578	8.483	1.15	1.22
4	5.471	5.813	7.768	8.254	1.42	1.42
8	4.445	4.716	7.512	7.262	1.69	1.54
12	3.576	4.062	6.329	6.336	1.77	1.56
16	2.657	3.464	4.915	6.027	1.85	1.74
20	2.013	2.838	4.670	5.448	2.32	1.92

Mechanical properties

Table 2 presents the changes of mechanical properties at different degradation stages. The initial mechanical properties of the PLLA/BG composites studied were lower compared to the plain matrix polymer (PLLA). This is presumably due to the formed interior microholes and thus the increased discontinuity of the structure. There seems to be no chemical adhesion between the polymer and bioactive glass

Table 2 Changes of mechanical properties with degradation time for PLLA and PLLA/BG composites

Degradation time/week	Bending strength/MPa		Bending modulus/GPa		Shearing strength/MPa	
	PLLA	PLLA/BG	PLLA	PLLA/BG	PLLA	PLLA/BG
0	233.8 ± 8.3	153.9 ± 8.5	3.25 ± 0.15	3.59 ± 0.25	127.5 ± 3.5	95.1 ± 2.1
4	193.5 ± 7.3	129.2 ± 5.7	3.01 ± 0.24	3.30 ± 0.17	108.2 ± 2.7	80.4 ± 2.4
8	157.2 ± 5.1	104.5 ± 5.1	2.77 ± 0.18	3.10 ± 0.21	89.3 ± 2.9	66.8 ± 1.7
12	115.7 ± 5.7	87.2 ± 5.3	2.56 ± 0.22	2.99 ± 0.20	73.4 ± 2.1	58.4 ± 1.5
16	91.5 ± 3.9	72.4 ± 4.2	2.44 ± 0.14	2.89 ± 0.17	65.4 ± 1.7	49.5 ± 1.8
20	74.2 ± 4.2	58.2 ± 3.9	2.32 ± 0.13	2.84 ± 0.20	59.8 ± 1.5	46.4 ± 1.4

particles, which also decreases the initial mechanical properties. The machining doesn't influence the initial mechanical properties of the composites.

The bending strength, shearing strength and bending modulus of the PLLA sample decreased with an increase in the degradation time and reaches 31.7, 46.9 and 71.4%, respectively, after 20 weeks of degradation; however, that of the PLLA/BG composite decreased to 37.8, 48.8 and 79.1%, respectively. Although the initial mechanical properties of the PLLA/BG composites were lower, they retained the properties in vitro longer than PLLA samples. The microholes and polymer/particle interfaces probably enable the degradation products of the matrix polymer also to diffuse away from the internal structure. The degradation products of PLLA are acidic and thus cause a local acidic environment in the interior of the implant which may catalyze further degradation.

The molecular weight and entanglements of the chains certainly affect the mechanical properties of the polymer greatly [19]. During the hydrolysis of PLLA, both the molecular weight and the number of entangled chains decreases, causing a decrease in the breaking force of the sample. That means the mechanical properties become poor after degradation.

It is known that the surfaces of PLLA samples are susceptible to corrosive degradation in an alkalescent environment [5]. The hydroxyl ion product of bioactive glass would inhibit the hydrolysis of PLLA; while, the local alkaline microenvironment it created at the PLLA/BG interfaces would erode the surfaces of the PLLA matrix and make the polymer surfaces coarser. Cracks are first caused by the breaking of the weak intermolecular van der Waals force and hydrogen bonding in the transversal direction of the matrix. After that, since the inter-macromolecular interactions are weakened with the time of in vitro degradation, the cracks expand continuously and penetrate into the inside of the matrix. Consequently, the material's tensile properties decrease.

Morphological changes of PLLA and PLLA/bioactive glass composites

The visual characterization of the samples in vitro showed that PLLA samples were initially transparent, but turned white and opaque during hydrolysis. The change was observed after 12 weeks in vitro. The PLLA/bioactive glass composites were white and opaque throughout the hydrolysis.

To obtain a micromechanistic understanding of the processes involved, the microstructures and fracture surfaces of the PLLA/BG and PLLA samples were examined before and after in vitro degradation using scanning electron microscopy, which provided further information on the morphology of surfaces of the samples after degradation. SEM micrographs of the sample surface before and after different periods of degradation in PBS are shown in Fig. 5. The morphology of PLLA material was smooth before degradation. As degradation continued, microholes and microcracks appeared on the PLLA sample surfaces. In addition to the cracks, various regions showed evidence of erosion. After 20 weeks of degradation, large cracks appeared on the PLLA surfaces and traces of partial material falling off can be observed. Cracks were first caused by the breaking of the weak intermolecular van der Waals force and hydrogen bonding. After that, since the inter-macromolecular interactions were weakened with the time of in vitro degradation, the cracks expanded continuously and penetrated into the inside of the polymer [20].

Comparing Fig. 5b and d, one can see that crack on the surface of the PLLA sample is larger than that on the surface of the PLLA/BG sample, but the surface of the PLLA/BG sample is coarser. It is known that the surfaces of the degradable polymer are susceptible to corrosive degradation in an alkalescent environment. The alkaline product of bioactive glass degradation would inhibit the hydrolysis of PLLA; while, the local alkaline microenvironment it created at the PLLA/BG

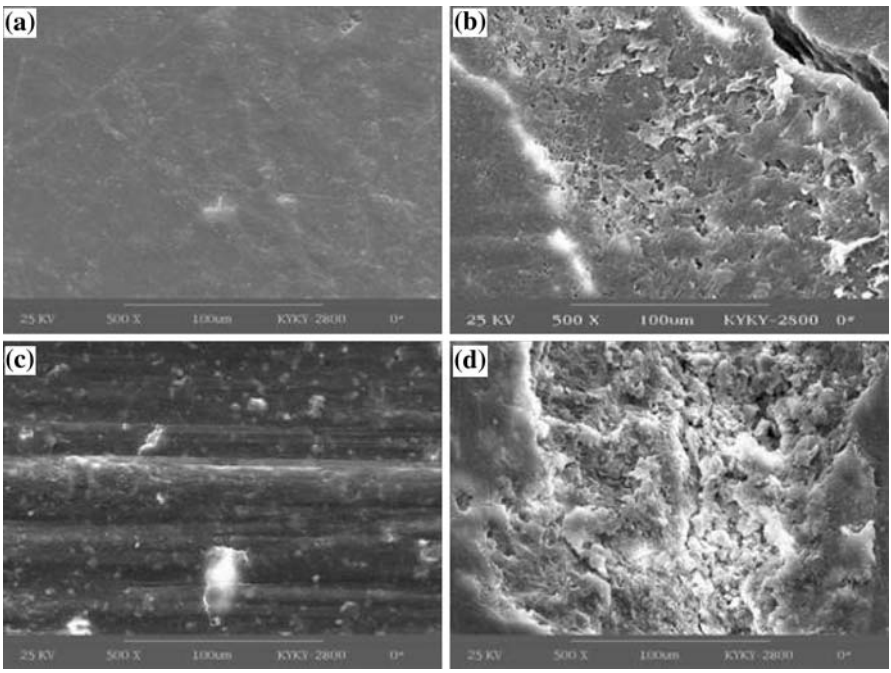

Fig. 5 SEM image of degraded samples surface: **a** PLLA before degradation; **b** PLLA for 20 weeks; **c** PLLA/BG before degradation; **d** PLLA/BG for 12 weeks

interfaces would erode the surfaces of the matrix and make the matrix surfaces coarser [20].

The morphologies of PLLA fracture are shown in Fig. 6. The morphology of the fracture surface of PLLA (Fig. 6a) exhibited a ductile fracture, with a lot of corrugation produced by the deformation of the PLLA matrix. After 4 weeks of degradation, no significant morphological changes were observed. After 12 weeks distinct alterations such as the appearance of cracks occurred. After 20 weeks, in addition to the cracks, large number microholes with diameter of 0.1–1.0 μm were observed (Fig. 6b); a small difference between the central region and the edges became pronounced. For PLLA/BG samples before degradation (Fig. 6c), a typical morphology of brittle failure with a smooth fracture surface was observed; bioactive glass particles in the PLLA matrix were homogeneously dispersed. After 20 weeks of degradation, a large number of cracks and microholes were observed, however, the cracks and microholes were smaller than that of the fracture surface of PLLA samples, which indicated that there was an obvious decrease in the degradation rate of PLLA/BG composite in the phosphate-buffered solution compared with sole PLLA samples. This is in agreement with the changes of mechanical properties during the different degradation period. A similar slower degradation rate was observed, for example, in coral/PLA50 composites [21].

The presence of the bioactive glass particles created pores and interfaces that facilitated the exchanges of acidic degradation products between the external

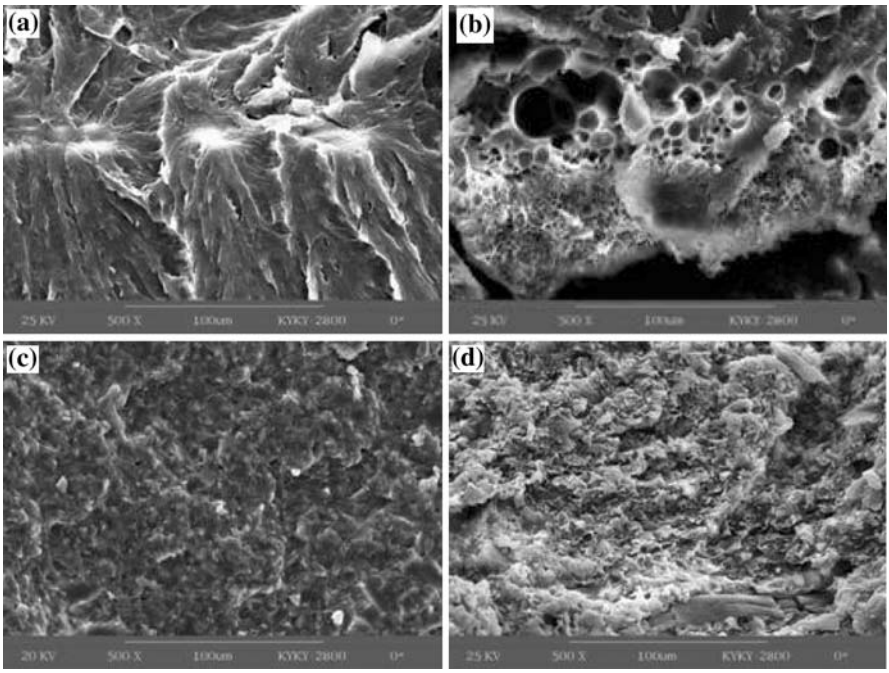

Fig. 6 SEM image of degraded samples cross-section: **a** PLLA before degradation; **b** PLLA for 20 weeks; **c** PLLA/BG before degradation; **d** PLLA/BG for 12 weeks

medium and the interior of the samples. The acidic degradation products were also neutralized by the alkaline degradation products of the bioactive glass particles and the autocatalytic effect of the matrix polymer was thus eliminated.

All results showed that the addition of the bioactive glass particles modified the in vitro degradation behavior. The plain matrix polymer, PLLA, followed a typical degradation behavior for semicrystalline poly-α-hydroxyacids [7]. The molecular weight started to decrease as soon as the samples were immersed in a buffer solution. The understanding of the effect of the added compounds on the matrix degradation is important, especially for materials intended for use as implant materials. Usually the degradation behavior is specific to each filler/matrix material combination and it is hard to predict. It depends on various factors, such as the filler content and interactions between filler and matrix materials as well as microstructural, macrostructural and environmental factors. It is important to design microstructures where the degradation rate matches the rate at which bone is formed at the implant site so that the material remains stable during its useful life.

Conclusions

Through the analysis of the results of in vitro degradation of the PLLA/BG composite material, it has been found that compared with sole PLLA material; there is an obvious decrease in the degradation rate of PLLA/BG composite in the phosphate-buffered solution. This can be explained that the acidic degradation products of the matrix polymer were neutralized by the alkaline degradation products of bovine bone particles and the autocatalytic effect of the matrix polymer was thus eliminated.

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