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# Modification of poly(L-lactic acid) with L-lactic acid / citric acid oligomers

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**Abstract:** The surface modification of polymeric biomaterials can be achieved by surface immobilization of bioactive molecules, increased hydrophilicity, and balanced hydrophilicity and hydrophobicity. Poly (L-Lactic Acid) (PLLA) is hydrophobic and possesses no reactive groups in the structure. In the present work, an effort has been made to blend PLLA with functionalized L-lactic acid / citric acid oligomer (PLCA) in order to improve the hydrophilicity of the PLLA. The compatibility of PLLA and PLCA was studied by using differential scanning calorimetry (DSC). The blends were also characterized for their water absorption, contact angle, tensile strength and hydrolytic degradation. The DSC results showed that PLLA/PLCA blends exhibited a single glass transition temperature (Tg), which lies in between that of PLLA and PLCA, thus asserting compatibility at the molecular level. The studies on water absorption, contact angle and hydrolytic degradation showed that addition of PLCA to PLLA enhanced the hydrophilicity of PLLA.

## Introduction

The development of new biomaterials for medical applications is one of the challenging tasks for materials science today. There is an obvious need for better implants as well as for the manufacturing of artificial tissues. Aliphatic polyesters such as polylactide (PLA), polyglycolide (PGA) and their copolymers (PLGA) are widely used as scaffolds and bioabsorbable implants. However, these materials have poor hydrophilicity and are devoid of cell recognition sites on their surfaces, which lead to poor mass transport in scaffolds and poor cell affinity of the materials. To improve the cell affinity of aliphatic polyesters, many efforts have been directed to modify their surface properties by adjusting the hydrophilicity / hydrophobility [1□2], surface energy [3], surface charge [4] and surface roughness [5, 6]. One of the possible and promising approaches to overcome this problem is to introduce hydrophilic functional segments or groups into the aliphatic polyester. Rouhi et al. has [7] studied about the self-assembled monolayer (SAM) of the PLA that was terminated with carboxyl functional groups and attached fibroblast cells to it in the proteinaceous environment of culture medium. They found that the attached cells grow and spread substantially better on a carboxyl terminated hydrophilic surface than on a methyl-terminated hydrophobic surface. The cholesterol-(L-lactic acid)$_n$ (CLAn) oligomers were synthesized by Klock et al. [8]. They found that the cholesterol moiety not only

induced liquid crystal properties and drives the self-assembly of the oligomers, but also affected the interactions between the cells and the oligomers. We have synthesized oligomers of poly (L-lactic-co-citric acid) (PLCA) from L-lactic acid and citric acid [9] and multiblock copolymers based on L-lactic acid, citric acid and poly (ethylene glycol) [10]. The carboxyl groups were introduced for immobilizing or entrapping bioactive species. Citric acid was selected because of the possibility that some of the complications resulting from the accumulation of lactic acid may be controlled to some extent, since the accumulation of lactic acid in the body is resulting from the inadequacy of oxaloacetic acid, which is the last product of the tricarboxylic acid cycle from citric acid.

Blending of polymers is a relatively simple and more cost-effective method as compared with copolymer synthesis to modify polymer properties, and it can represent, in some cases, an alternative to copolymerization. Generally, blends exhibit advantageous physical and chemical properties that each individual polymer does not possess. If an opportune second component is selected, a tailor made material with some specific properties can be obtained. A number of studies have focused on the bending of PLA with other polymers or copolymers [11, 12]. These blends include PLA with PHB [13], blends of PLA with PEG [14-16] and blends of PLA with chitosan [17-18], dextran [19], poly( ε-caprolactone) [20-21] etc. Properties of blends depend not only on the chemical composition of the blend but also on the compatibility or miscibility of the components. The PLGA scaffolds were prepared by blending PLGA with varying amounts of amine-terminated PLGA-PEG di-block copolymer. Hyaluronic acid (HA) was chemically conjugated to the surface-exposed amine groups on the pre-fabricated scaffolds. When chondrocytes were seeded within HA modified PLGA scaffolds, enhanced cellular attachment was observed compared to unmodified PLGA scaffolds. Furthermore, glycosaminoglycan and total collagen synthesis increased substantially for HA modified PLGA scaffolds [22].
In the present study, the blends from PLLA and PLCA with different ratio of PLCA were prepared by solution casting. The compatibility of PLLA and PLCA was evaluated by DSC. The surface and bulk properties of the blends, such as hydrophilicity, mechanical properties, swelling and hydrolytic degradation behavior were also investigated.

## Results and discussion

### *Compatibility*

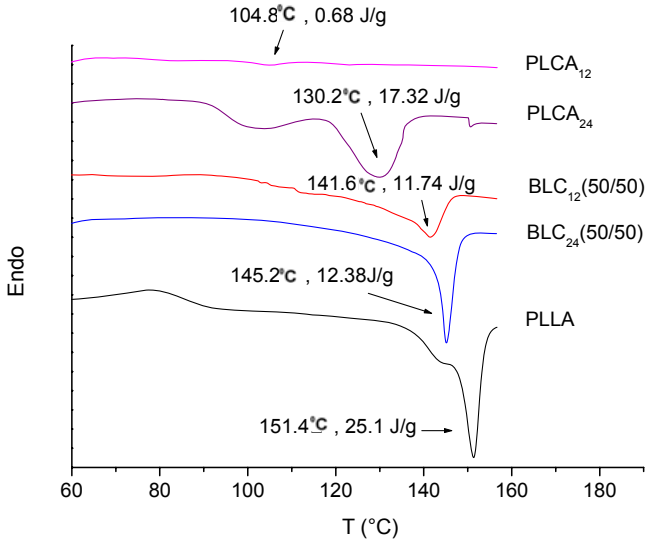
**Tab. 1.** Physicochemical properties of PLCAs.

| | $\overline{Mn}$ | | LA/CA (mole ratio)[a] | | [COOH]×10$^3$ (mol/g)[b] | |
|---|---|---|---|---|---|---|
| | $^1$H-NMR | $\overline{Mw}/\overline{Mn}$ (GPC) | feed | oligomer | Cal | Exp |
| $PLCA_{12}$ | 1381 | 1.477 | 12 | 19.57 | 1.98 | 1.96 |
| $PLCA_{24}$ | 2093 | 1.462 | 24 | 28.46 | 1.40 | 1.41 |

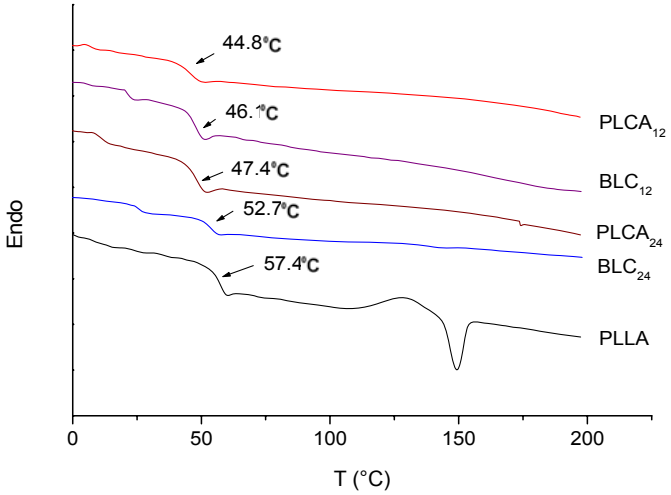
[a] Mole ratio of lactic acid to citric acid units in PLCAs was determined through $^1$H-NMR analysis [9].

[b] Carboxyl terminal groups of PLCAs were determined by titration in 1:1 (volume) methanol and dichloromethane solution of the samples with 0.05 mol/l KOH in ethanol. Bromothymol blue was used as the indicator [9].

PLCAs exhibit some different properties depending on the molar ratio of lactyl to citryl units in their cooligomers.




(a)*




(b)*

**Fig. 1.** DSC curves of PLLA, PLCAs and blends.

*(a) As-prepared samples; (b) The second run curves were obtained after quenching the samples using liquid nitrogen

Tab. 1 lists the physicochemical properties of the two kinds of PLCAs used in this study. The thermodynamic compatibility between PLLA and PLCA is expected to be excellent. Indeed, the PLLA/PLCA blend films are all translucent, indicating the miscible structure. However, the physical appearance of the blend film is only indirectly indicative of polymer compatibility. DSC studies are carried out to examine the compatibility between PLLA and PLCA. Although the main units of lactic acid of PLLA and PLCA are the same, introducing citric acid (from PLCA) into the blend may disturb the crystal behaviors of PLLA. Thus, the decrease of crystallinity and glass transition temperature of PLLA in PLLA/PLCA blends can be expected. The DSC

curves are presented in Fig. 1 and the thermal properties of the blends are listed in Tab. 2. A shift in glass transition temperature ($T_g$) provides direct evidence of polymer compatibility while PLLA, $PLCA_{24}$ and $PLCA_{12}$ has a clear $T_g$ around 57.4, 47.4 and 44.8□ respectively, the PLLA/PLCA blends exhibit a single $T_g$ which lies between the $T_g$ values of PLLA and PLCA, suggesting the disturbed amorphous region of PLLA by the PLCA, which may act as a plasticizer.

**Tab. 2.** Thermal properties of PLLA/PLCA blends

| Property | PLLA | $PLCA_{12}$ | $PLCA_{24}$ | $BLC_{12}$ | $BLC_{24}$ |
|---|---|---|---|---|---|
| $X_{PLCA}$ | 0 | 100 | 100 | 50 | 50 |
| $T_g$ (°C) | 57.4 | 44.8 | 47.4 | 46. 1 | 52.7 |
| $T_m$ (°C) | 151.4 | 104.8 | 130.2 | 141.6 | 145.2 |
| $\Delta H_m$ (J/g) | 25.1 | 0.68 | 17.32 | 11.74 | 12.38 |

The crystalline melting temperatures ($T_m$) of the blends are also used to evaluate the extent of compatibility. Fig. 1 also shows that the blends exhibit a single melting point ($T_m$). This signifies that the two polymers are miscible in the crystalline phase or in other words, they are isomorphous. This type of behaviour in polymer blends is very rare as it requires that the components of the blends should have close matching of chain conformations, lattice symmetry and crystallization kinetics. In the present case, isomorphous behaviour results from the fact that the unit cells of PLLA and PLCAs are very much identical owing to the similarity in their structure. So in the solution-cast blends (first run), as the solvent evaporates, chains of both polymers arrange themselves into the same lattice as crystallization progress, since the chains of the two polymers are virtually interchangeable in the crystal lattice.

As shown in Fig. 1 (a), the PLLA sample exhibits a melting peak at 151.4 °C, 25.1 KJ/mol, and $PLCA_{12}$ and $PLCA_{24}$ show a relatively wider melting peak at 104.8 °C, 0.68 KJ/mol and 130.2 °C, 17.32 KJ/mol. The melting peaks of $BLC_{12}$ (50/50) and $BLC_{24}$ (50/50) shift to about 141.6 °C, 11.74 KJ/mol and 145.2□, 12.38 KJ/mol, a more significant shift in $T_m$ of PLLA is observed upon blending $PLCA_{12}$ than $PLCA_{24}$. The crystalline melting enthalpy ($\Delta H_m$) data show the higher crystallinity values in blends of $PLCA_{24}$ than in $PLCA_{12}$. Since $T_m$ is related to crystalline structure and size and $\Delta H_m$ to crystallinity, this result implies that the percentage of citryl units in PLCA appears to affect the nucleation and growth of crystalline spherulites. As reported earlier [10], the citryl units of PLCA are mainly located at the chain ends; the crystal structure of PLCA is very similar to that of PLLA. On the other hand, the crystallinity of PLCA decrease resulting from the steric hindrance of citryl units. Hence the lower the mole ratio of lactic acid to citric acid in PLLA/PLCA blends, the smaller the crystallinity and crystalline size.

However, DSC traces change completely in the second scan taken after quenching from the melt to -150 °C for the solution cast blends. As can be seen in Fig. 1 (b), except PLLA, all the melting endotherms in the first run disappear for PLCAs and BLCs. PLLA gives a small exothermic peak of crystallization at 128 °C followed by a single endothermic peak. When the samples are quenched after melting, an integrate amorphous state is fixed. In the second run, the crystallization and melting behavior depend on the rate of heating and crystallization. For PLCAs and BLCs, the volume resistance of citryl units makes them more difficult to crystalline than PLLA, so the

crystallization for PLCAs can hardly occur at a heating rate of 10 °C/min. However, solution casting techniques can induce crystallization, even in systems that are normally amorphous [23]. In the first run, all the as-prepared samples have melting peaks.

### *Tensile strength*

It is known that the mechanical properties of a polymer blend depend not only on the mechanical properties of each component but also on their compatibility. For the blends investigated in the present study, the relationships between the tensile strength and the weight percentage of PLCAs ($X_{PLCA}$) are shown in Fig. 2. For both of the $BLC_{12}$ and $BLC_{24}$ blends, the tensile strength decreases monotonously with the increase of the amount of PLCAs. The DSC analysis demonstrates the good compatibility between PLLA and PLCA, and PLCA acts as a plasticizer. The mechanical properties of PLCA oligomers are relatively poor. The molecular weight and crystalinity of $PLCA_{24}$ is a little higher than $PLCA_{12}$ [9], so $BLC_{24}$ has a higher tensile strength than $BLC_{12}$ blends.

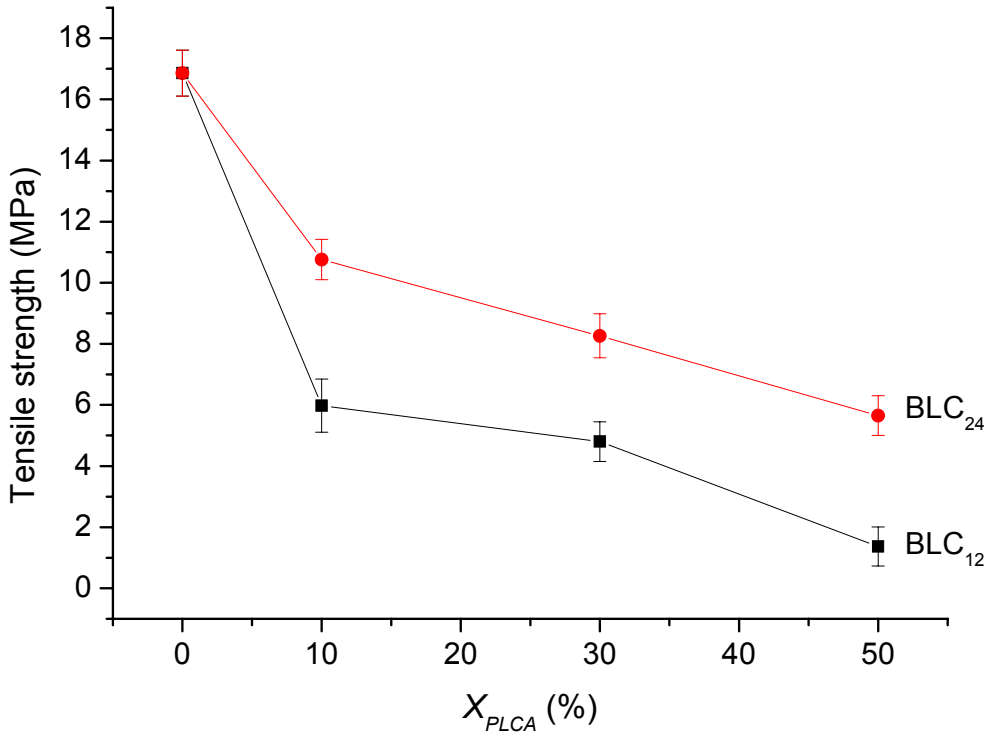



**Fig. 2.** The tensile strength of PLLA/PLCA blend films as a function of $X_{PLCA}$.

### *Hydrophilicity*

The contact angles of the blend films are plotted in Fig. 3 as a function of the $X_{PLCA}$. The average contact angles for nonblended PLLA, $PLCA_{24}$ and $PLCA_{12}$ are 114, 62 and 41° respectively. Evidently the contact angle decreases monotonously with a rise in the $X_{PLCA}$ of the blend films. This strongly suggests the probability that the hydrophilicity of the biodegradable materials based on the PLLA family can be controlled by the addition of relatively hydrophilic biodegradable polymers. On the other hand, the experimental values of the contact angles of the blend films from PLLA and PLCA are lower than those expected from nonblended PLLA and PLCA

films. This implies that the surface concentration of PLLA and PLCAs are different from those of their bulk concentrations. In other words, the enrichment of the PLCAs occurred at the surfaces of the blend films during solvent evaporation. Comparing with $PLCA_{24}$, $PLCA_{12}$ contains more citryl units and carboxyl acid groups, so the $BLC_{12}$ blends have smaller contact angles and more significant surface enrichment effects of PLCA than $BLC_{24}$ blends.

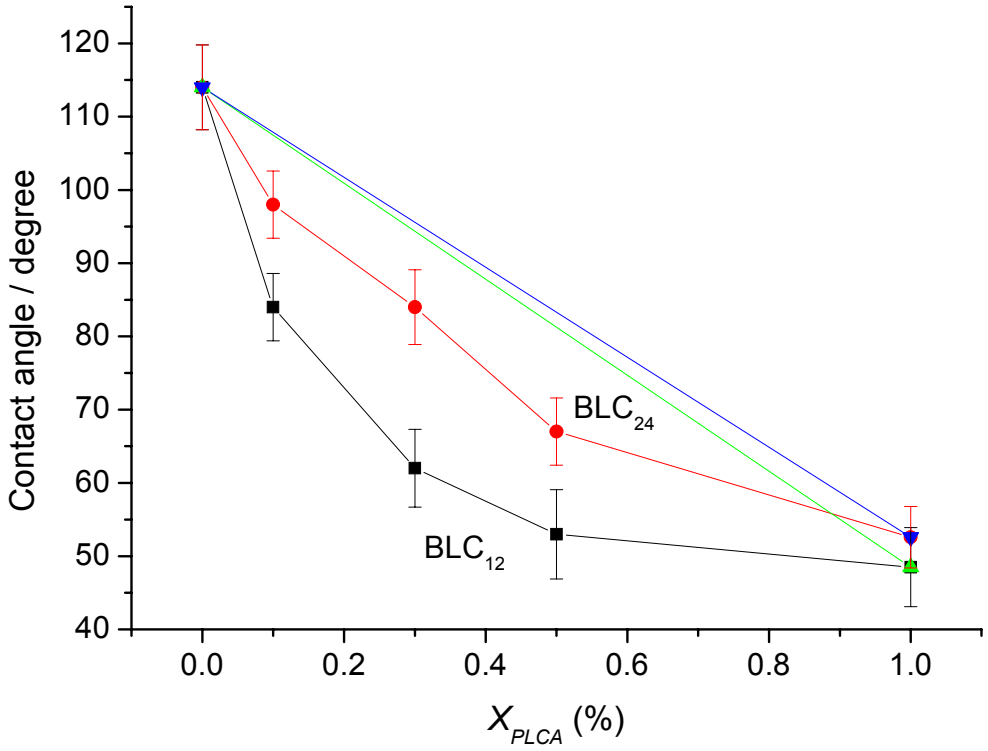



**Fig. 3.** Contact angles of PLLA/PLCA blends.

### *Hydrolytic degradation*

A typical biodegradable PLLA is relatively hydrophobic and it has a semicrystalline structure. Degradation proceeds via nonenzymatic, hydrolytic breakage of the ester backbone bond. Water accessibility to these bonds will determine the rate of degradation. It takes months to years for complete degradation of PLLA matrices, depending on the molecular weights [24]. Blending PLLA with PLCA is expected to produce matrix with different degrees of hydration depending on the choice and amount of PLCAs. Thus, one can expect that degradation will be accelerated by a high water concentration in the vicinity of the hydrolytically labile ester bond. In this study, a variety of blend films, $BLC_{12}$ and $BLC_{24}$ are prepared.

Fig. 4 shows the hydration degree for blends of PLLA with PLCAs as a function of incubation time for different $X_{PLCA}$ in PBS, pH 7.4 at 37□. All blends show high water content relative to the homogeneous PLLA; the water content increases with increasing amounts of PLCAs in the blends. The equilibrium hydration degree $A_w$ of PLLA is about 11.7%, the $A_w$ values of $BLC_{24}$ are 19.1, 26.9 and 39.2 corresponding to the blends with 10, 30 and 50 weight percent of $PLCA_{24}$. The values of $A_W$ are 23.0, 49.1 and 53.3 corresponding to the blends with 10, 30, 50 weight percent $PLCA_{12}$. So the more hydrophilic $BLC_{12}$ blends exhibit higher water contents than the

$BLC_{24}$ blends.

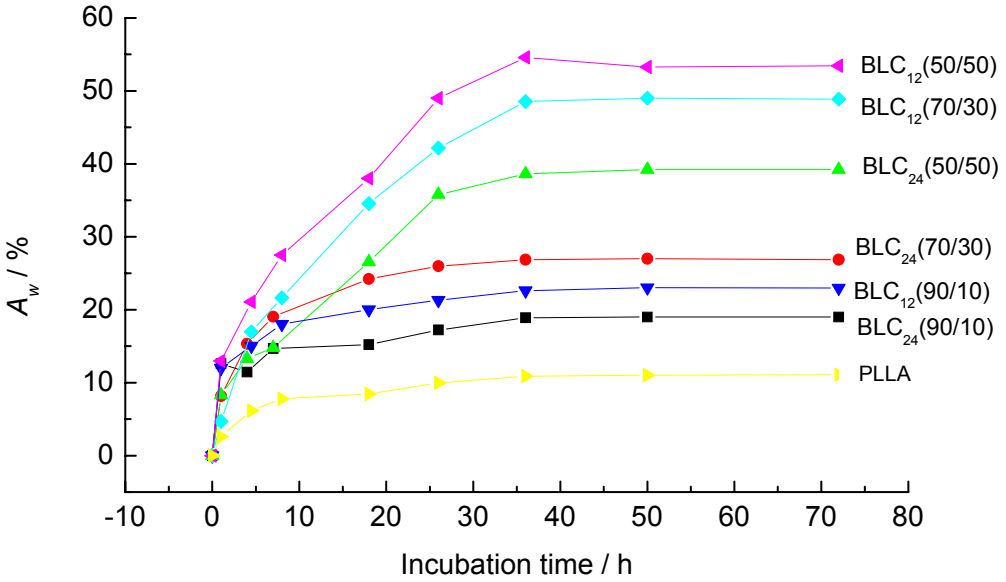



**Fig. 4.** The hydration degree for blends of PLLA with PLCAs

PLLA has been known to degrade slowly because of its hydrophobic and semicrystalline structure which does not allow fast water penetration. The degradation rate is proportional to water and ester concentrations and is autocatalyzed by the generated carboxylic end groups. In our hydrolytic degradation experiments, weight loss is investigated for different blend films as shown in Fig. 5 and Fig. 6.

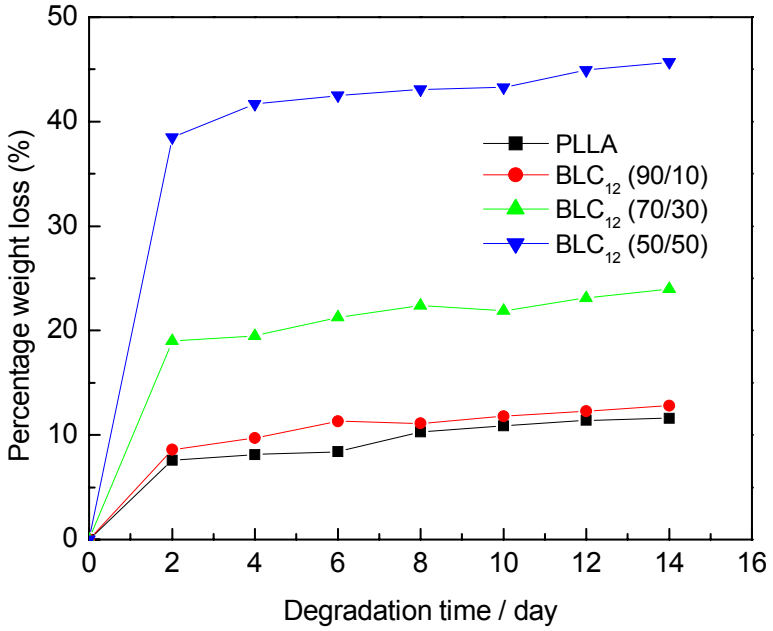



**Fig. 5.** Weight loss during hydrolytic degradation of $BLC_{12}$ blend films.

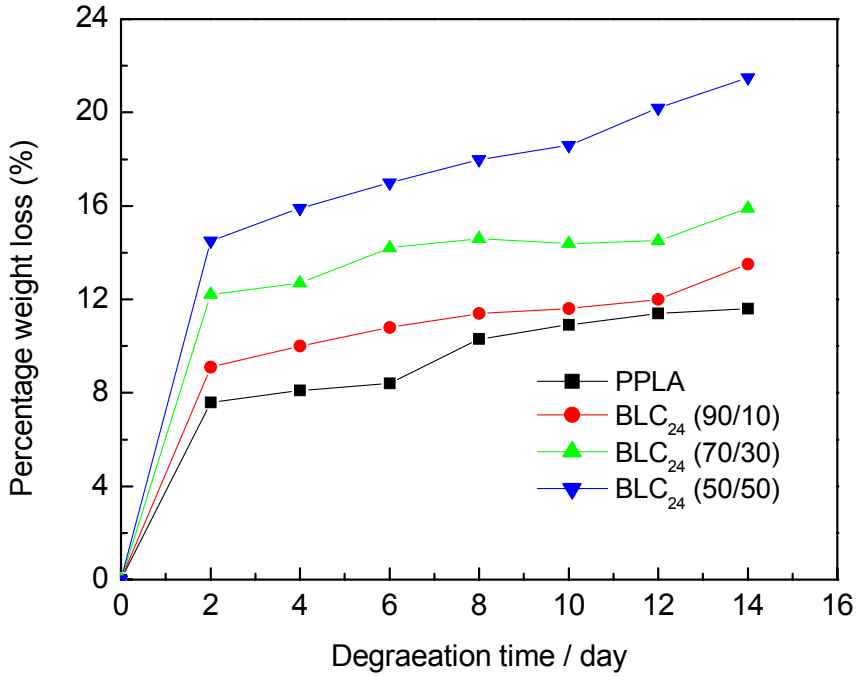



**Fig. 6.** Weight loss during hydrolytic degradation of $BLC_{24}$ blend films.

It is interesting to note that same trend is observed in both cases that the hydrolytic degradation increases dramatically at first (during two days of degradation) and then smoothly for the following days. Both the degradation of PLLA or PLCA and the dissolution of the degraded products contribute to the weight loss of the blends. The mole ratio of lactic units to citric units of the blends after degradation is shown in Fig. 7.

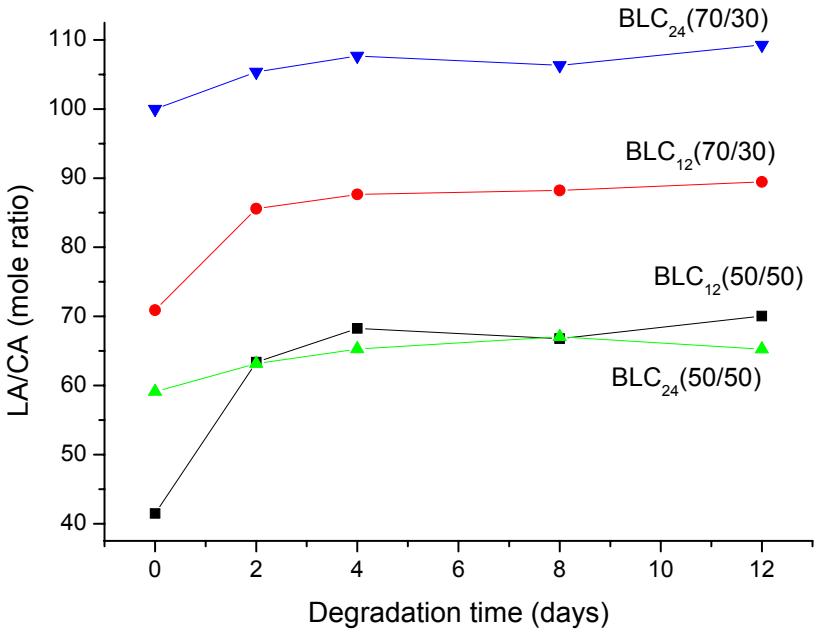



**Fig. 7.** Relationship between the mole ratios of LA/CA of the blend films with degradation time.

For the blend of $BLC_{12}$ with 50 weight % $PLCA_{12}$, the mole ratio value of LA/CA enhanced from 59.11 to 63.17 after 2 days, the total mass loss is 38%. Hence the rapid weight loss at the beginning can be attributed to low molecular weight of PLCA and high carboxyl group contents in PLCAs molecular chain. Consequent decrease of mass loss ratio reveals that the effect of PLCAs is not the domain factor but the degradation product of PLLA instead, because the molecular weight of the degraded polymers (see Fig. 8) is not low enough to dissolve from blend during the degradation period. Schliecker et al. [25] determined the solubility of various polydisperse oligo(D, L-lactic acid)s via direct measurements. It was found that the solubility of oligomers depends on both pH and average molecular weight. Oligo(D, L-lactic acid)s with $M_n$ smaller than 830 are soluble in buffer at pH 7.4 whereas oligomers of $M_n \geq 830$ are insoluble.

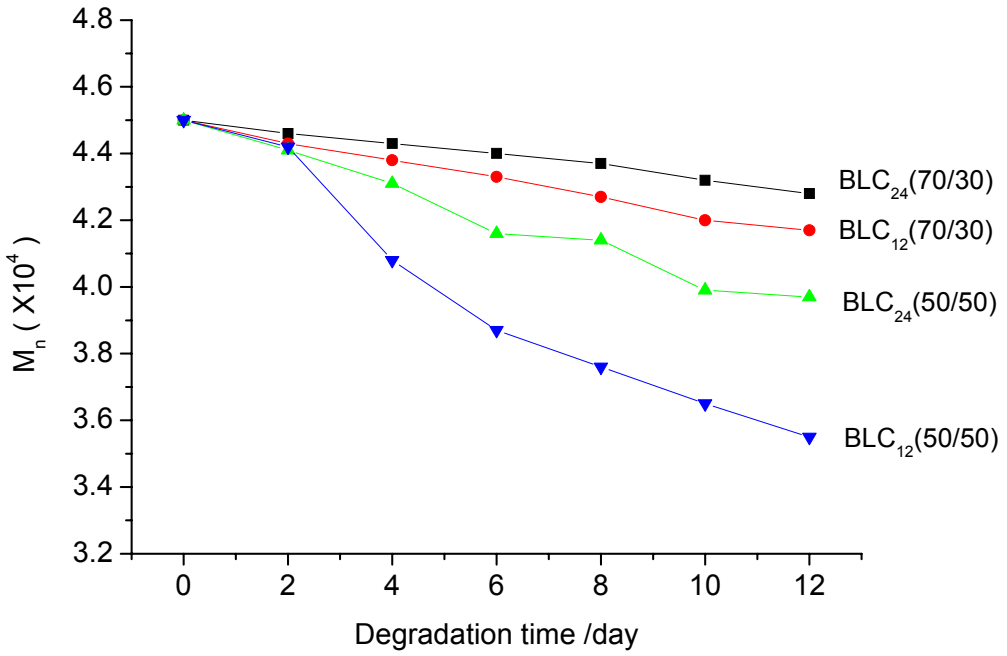



**Fig. 8.** Molecular weight changes of PLLA in blends during hydrolysis degradation

PLA degrades by several mechanisms, random scission within the polymer and backbiting of the terminal hydroxyl ends. Moreover, the carboxyl ends promote degradation by polarizing ester bonds and providing acid groups that accelerate the rate of hydrolysis. The carboxyl groups attract and become surrounded by water molecules that promote degradation. The fact that the blends containing more PLCAs loss the molecular weight faster, suggests an acceleration of the degradation process (Fig. 8). This can be explained again by the enhancement of the water penetration resulting from the higher hydrophilicity of PLCAs than PLLA in the blends. Also the faster reduction in molecular weight of PLLA in $BLC_{12}$ as compared to that in $BLC_{24}$ can attributed to the same reason. From Fig. 9, it is clear that the weight loss of the blends after incubation in PBS for 48 hours enhances as the amount of PLCAs increases. Compared with $BLC_{24}$, the blends $BLC_{12}$ exhibit faster weight loss rates because of their higher hydrophilicity and carboxyl group content. The weight loss of $BLC_{24}$ with 50% $PLCA_{24}$ is 13.8% after 48 h, otherwise 38.2% for $BLC_{12}$ (50/50).

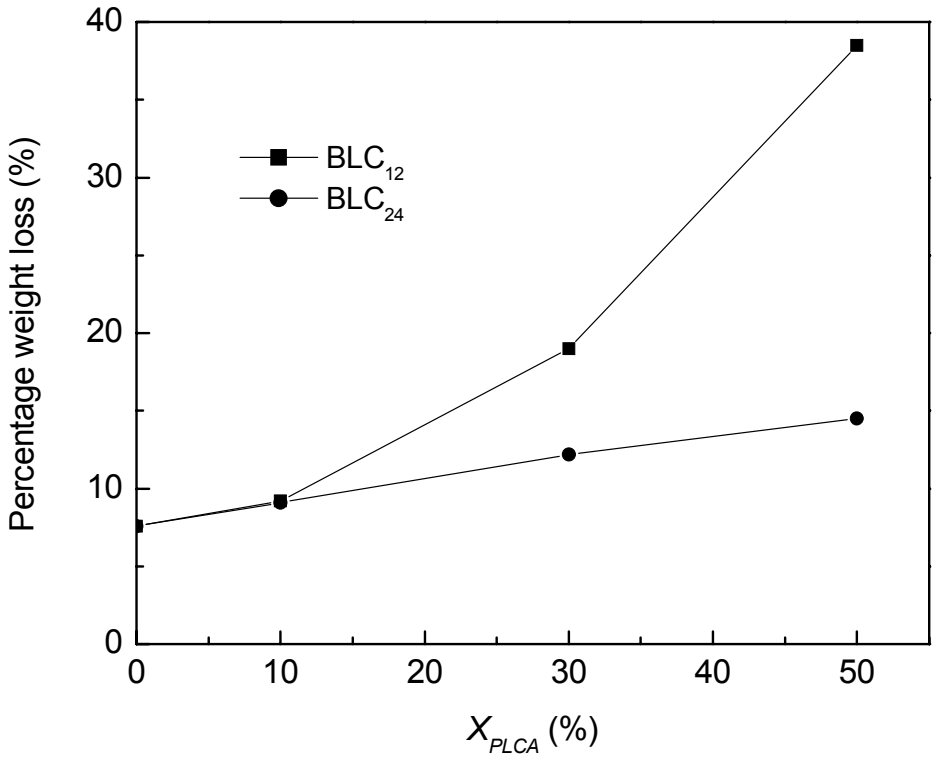
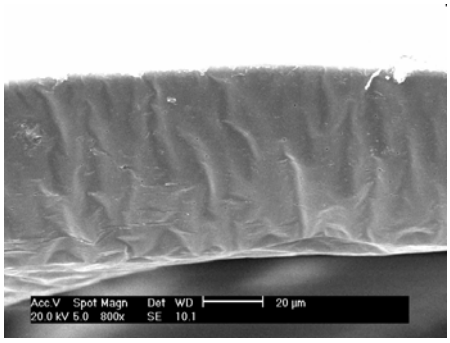
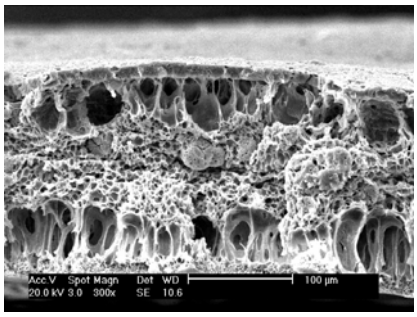


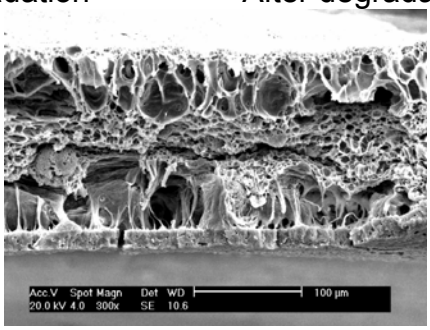

**Fig. 9.** Weight loss of PLLA/PLCA blend films after incubation in PBS for 48 hours.



Before degradation



After degradation (2 days)



After degradation (14 days)

**Fig. 10.** Scanning electron micrographs of the fracture surfaces of a hydrolytically degraded $BLC_{12}$(50/50) film

Fig. 10 shows SEM photographs of the blends of $BLC_{12}$ (50/50) which obtained by hydrolyzing in PBS for 2 and 14 days followed by cooling in liquid nitrogen. The undegraded blend shows a smooth, homogeneous fracture surface, while the hydrolytically degraded blend shows the formation of pores. Both the amount and the size of the pores in the film increase from the inside to the surface during the hydrolytic degradation, which implies that the weight loss of the blends resulting from the degradation of PLCAs and partial diffusion of the oligomers occurs from the surface to the inside. This is consistent with the results of contact angle analysis, which indicated an enrichment of PLCA on the surface during solvent evaporation. The appearance of the samples was transparent but they turned white after several days of degradation. This whitening is the result of void formation owing to the dissolution of degraded PLCA or PLLA.

## Conclusions

Multicarboxylated poly (L-lactic-co-citric acid) oligomers were synthesized and blended with PLLA. A single $T_g$ and $T_m$ for the blends containing up to 50% PLCAs, which is in between that of the pure components indicated that PLCA and PLLA are compatible.

The mechanical properties of the blends are significantly influenced by blending with PLCA. The tensile strength of the blends decreased because PLCA acted as a plasticizer. Contact angle and hydration studies showed that the hydrophilicity of the blends depends on the ratio of PLCA to PLLA. The initial degradation rate of the blends is faster than that of unblended PLLA. A major problem in the use of PLLA in biomedical application is its very low degradation rate, hydrophobicity and lack of reactive groups. Blending PLLA with PLCA could therefore be a convenient way to improve its hydrophilicity and degradation behavior. The carboxyl groups of PLCA could be used to immobilize bioactive molecules on the surface of PLLA based devices. Suitable applications on research of these blends as tissue engineering scaffolds are going on.

## Experimental

### *Materials*

The synthesis and characterization of PLCA were described in detail in the previous articles [9, 10]. An 88% aqueous solution of L-lactic acid was added into a three-neck flask with citric acid under a nitrogen atmosphere and mechanical stirring. The temperature was gradually raised to 140-150 □, first at atmospheric pressure for 3 h, further at a reduced pressure of $1.3\times10^4$ Pa for 2 h, and finally under $1.0\times10^3$ Pa of pressure for 3 h. Then the nitrogen flow was discontinued and about 0.4 wt% of stannous chloride was added and a high vacuum was applied for another 8 h. The resulting product was dissolved in acetone and then precipitated in distilled water. After washing with a large amount of water for several times, the polymer powder was collected and dried in a vacuum oven for 48 h. The products $PLCA_{12}$ and $PLCA_{24}$ were obtained (subscription 12 and 24 represent the feed mole ratio of L-lactic acid to citric acid). PLLA was obtained through ring-opening reaction of lactide as usual. L-lactide was purified by repeated recrystallization using ethyl acetate as solvent. Ring-opening polymerization was performed for L-lactide in bulk at 140 □ for 48 h, using stannous octate (0.02 wt %) as the polymerization catalyst. The resulting polymer was purified by reprecipitation using chloroform as solvent and methanol as

the precipitant. $M_n$ of PLLA is $3.0\times10^4$ ($^1$H-NMR) and $M_w/M_n$=2.2 (GPC).

### *Preparation of the samples*

Solution blending was used in this study. PLLA and PLCA were dissolved in chloroform (10 wt%) and they were blended by stirring to form a uniform solution. The resulting solutions were poured into Teflon trays followed by solvent evaporation at ambient temperature for approximately 24 h, then dried for 12 h at a pressure of $5\times10^4$ Pa, finally at 27 Pa until the weight remained stable. The average membrane thickness was about 0.14 mm, and then tailored into 10 mm×20 mm. The component codes of each blends are summarized in Tab. 3.

**Tab. 3.** Composition and codes of PLLA/PLCA blends.

| Codes | PLLA (wt%) |
|---|---|
| $BLC_{12}$( 90/10) | 90 |
| $BLC_{12}$(70/30) | 70 |
| $BLC_{12}$(50/50) | 50 |

### *Measurements*

#### -Differential scanning calorimetry (DSC)

DSC measurements were conducted with DSC-2910 instrument (DuPont, America), under nitrogen atmosphere. Samples of 3~10 mg were sealed into aluminum pans under dry conditions. They were heated to 160 □ from 25 □ at 10 □/ min and the process was recorded in the first curve. Subsequently, they were quenched in stirred liquid nitrogen and heated from -150°C to 220°C at a rate of 10 °C / min; the second curve was recorded. The temperature and power scales of the calorimeter were calibrated by melting indium, and the temperature scale was checked against melting point standards. Apparent melting temperatures were obtained from the temperatures of the first curves at the peaks of the endotherms, and enthalpies of melting ($\Delta H_m$) were obtained from peak areas. Glass transition temperatures were obtained from the respective second curves. The midpoint of the slope change of the heat capacity curve was taken as glass transition temperature ($T_g$). The melting point of each endotherm was located in the maximum of their respective peaks.

#### -GPC

Gel permeation chromatography (GPC) experiments were performed to determine molecular weights and molecular weight distributions. The GPC system consisted of a Waters Alliance 2690 separation module, a Waters 484 tunable absorbance detector, an on-line multiangle laser light scattering (MALLS) detector (MiniDawn, Wyatt Technology Inc.), an interferometric refractometer (Optilab DSP, Wyatt Technology Inc.), and two 3 lm PLgel (Polymer Laboratories Inc.) columns connected in series. The system used THF as the mobile phase at a flow rate of 1 ml/min, and sample concentrations ranged from 7 to 10 mg/ml. The detector signals were simultaneously recorded, and the data were converted to absolute molecular weights

and molecular weight distributions using ASTRA software (Wyatt Technology Inc.).

### -SEM

The morphology of the blend samples before and after hydrolysis was investigated with XL30 (PHILIPS) scanning electron microscope at 20 KV electron beam radiation. The samples were fractured in liquid nitrogen and coated with gold particles to a thickness of 200-500 angstrom.

### -Contact angles

The contact angles of the films with water were determined on a Contact Angle Meter Phoenix 150. Blend films were cast from a 2% solution in chloroform over glass slides. After controlled evaporation of the solvent, all films were dried under vacuum at room temperature for one week to remove residual chloroform. Contact angles were measured by placing a sessile drop of liquid on the cast polymer surface with a micrometer syringe. The drop volume was gradually increased from 0.1 to 0.5 μl. The measurements were carried out at 25 $^0$C and the humidity was maintained at 28 %. Each value reported is an average of eight measurements.

### -Tensile strength

Measurements on mechanical properties of the blend films were performed at room temperature with a DZL-50 tensile testing machine at a cross-head speed of 10 mm/min. Each value reported is an average of five measurements.

### -Water absorption

The blend samples (10 mm × 20 mm) were incubated in phosphate-buffer solution (pH=7.4). At some definite time intervals, samples were taken out and washed by distilled water 3 times, taking the surface water away using filter paper and then weighed. The water absorption was evaluated using the following equation.

$$A_w\% = 100 \times (W_s - W_a) / W_a$$

Where $W_a$, $W_s$ are the film weights before and after immersion in water, respectively. Each value reported is an average of three measurements.

### -Hydrolytic degradation

Hydrolytic degradation of the samples (10 mm × 20 mm) was performed in 10 ml of 0.15 M of the phosphate-buffered and the solution was charged once in a week. The samples were taken out and washed intensively with distilled water, dried for 24 h at room temperature, followed by 48 h under reduced pressure (27 Pa) at 40 □. The weight loss percentage was evaluated according to the following equation:

$$\Delta W(\%) = 100 \times (W_0 - W) / W_0$$

where $W_0$ and W are the weight of the samples before and after hydrolytic degradation. Each value reported is an average of the three measurements.

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