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Poly(L-lactic acid)/SiO_2 nanocomposites via in situ melt polycondensation of L-lactic acid in the presence of acidic silica sol: Preparation and characterization

Linbo Wu*, Dan Cao, Yuan Huang, Bo-Geng Li

State Key Laboratory of Polymer Reaction Engineering, Department of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou 310027, China

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Abstract

In situ melt polycondensation of L-lactic acid (LLA) in the presence of acidic silica sol (aSS) is proposed for the first time to prepare PLLA/SiO_2 nanocomposites. The SiO_2 nanoparticles were readily dispersed in LLA monomer, which has similar polarity and hydrophilicity to the silica sol medium. During the polycondensation process, both the matrix and the surface of SiO_2 nanoparticles changed from high polarity/hydrophilicity to weak polarity/hydrophobicity due to simultaneous chain growth in the organic phase and chemical grafting on the particle surface. The chemical grafting provided steric stabilization and ensured satisfactory nano-scale dispersion in the final nanocomposites. The introduction of SiO_2 nanoparticles resulted in unchanged yield and better color. The molecular weight kept almost constant at low SiO_2 content (<8 wt%) but decreased at higher SiO_2 content. The method is also characterized by commercially available and cheap starting material and environmentally benign process. It appears to be a promising approach for the preparation of PLLA/SiO_2 nanocomposites.

Keywords: Poly(L-lactic acid); In situ melt polycondensation; Nanocomposites

1. Introduction

Poly(L-lactic acid) (PLLA) is one of most important and promising bio-based and biodegradable materials. It is produced from renewable resources such as cornstarch [1] and is biodegradable in natural compost or biodegradable and bioabsorbable in physiological environment, eventually being converted to carbon dioxide and H_2O. The polymer has tremendous market potentials [2] in packing materials, fibers, agricultural films and biomaterials [3,4]. However, some of its properties such as thermal stability, toughness and gas-barrier are still not satisfactory for various end-used applications. For properties' improvement, PLLA nanocomposites with layered silicates [5] have been extensively studied in recent years. PLLA nanocomposites with hydroxyapatite [6], carbon nanotube [7] and silicon dioxide (SiO_2) [8] have also been reported. The thermal, mechanical, gas-barrier, degradation and flame-retardant properties have been greatly improved [8,9].

Most of the PLLA nanocomposites are prepared by melt bending [10,11] or in situ ring opening polymerization of lactide [8,12–15]. In order to introduce appropriate interfacial interaction between the surface of the inorganic nanoparticles and the organic matrix and to reach nano-scale dispersion, the nanoparticles usually have to been modified before use [16,17]. But surface modification often results in extra cost and usage of toxic organic solvent, which is undesired due to environmental concern. Sol–gel technology is another means to prepare nanocomposites of PLLA [18] as well as other polymers [19–23], but expensive precursors and toxic solvent also have to be employed. The volatilization of solvent and small molecular by-product often results in shrinkage and stress cracking. It is usually hard to prepare bulky or thick nanocomposites with excellent properties.

A few articles have reported preparation of PLLA/SiO_2 nanocomposites by sol–gel method [18] using tetraethyl

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* Corresponding author. Tel.: +86 571 87952631; fax: +86 571 87951612.
E-mail address: wulinbo@zju.edu.cn (L. Wu).

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orthosilicate (TEOS) or in situ polymerization [8,14] using aerosil. Preparation of polymer/silica hybrid nanoparticles has also been reported [24]. In this study, we propose an in situ melt polycondensation strategy for PLLA/SiO_2 nanocomposites using acidic silica sol as the starting nanomaterial for the first time.

Silica sol is a dispersion of SiO_2 nanoparticles in aqueous (both alkaline and acidic) or organic media. They are commercially available and much cheaper than TEOS and aerosil, and therefore become very attractive starting inorganic nanomaterials for nanocomposites. Alkaline [25] and organic [26] silica sols have been applied in nanocomposites but few applications of acidic silica sol (aSS) in nanocomposite have been reported. In fact, aSS is stable enough at acidic aqueous medium (pH 2–4) and therefore is able to be stably dispersed in acidic monomer or its aqueous solution. The abundant silanol groups on the particle surfaces will provide potential sites for in situ chemical grafting. Therefore, it is an ideal starting nanomaterial for nanocomposites via in situ melt polycondensation of L-lactic acid.

In this report, PLLA/SiO_2 nanocomposites in which SiO_2 nanoparticles are well dispersed and chemically grafted with oligomers of LLA were successfully prepared via in situ melt polycondensation of LLA in the presence of aSS and characterized. The effects of SiO_2 nanoparticles on the melt polycondensation behaviors have also been examined.

2. Experimental part

2.1. Materials

L-Lactic acid (LLA) with optical purity of 98% was supplied as a 90 wt% aqueous solution by Jiangxi Musashino Corporation (China). Acidic silica sol (aSS) containing 25.4 wt% silicon dioxide (SiO_2) nanoparticles with average diameter 12 nm was purchased from Zhejiang Yuda Chem. Co. (China). Stannous chloride ($SnCl_2 \cdot 2H_2O$) and toluene-*p*-sulfonic acid (TSA, both A.R.) were used without further purification.

2.2. Dehydration/oligomerization

Eighty grams of aqueous solution of LLA was mixed with a predetermined quantity of aSS. The mixture was ultrasonically treated for 30 min before it was charged into a 250-mL three-necked flask equipped with a magnetic stirrer. The mixture was dehydrated at 110 °C and under atmospheric pressure for about 2 h and then ultrasonically treated again since it gradually changed from translucent to opaque during the dehydration process. After the second ultrasonic treatment, the dehydration operation was continued at 130 °C and under a reduced pressure of 10^4 Pa for 3 h, and then at 150 °C/400 Pa for another 4 h. Finally, a viscous product containing oligo-(L-lactic acid) and nano-silica (OLLA/SiO_2) was obtained.

2.3. In situ melt polycondensation

The 250-mL three-neck flask was re-equipped with a mechanical stirrer and a reflux condenser that was connected with a vacuum system to perform the melt polycondensation reaction. A predetermined amount of $SnCl_2 \cdot 2H_2O$ and TSA (1:1 molar ratio) was charged into the flask and used as a binary catalyst. The mixture was gradually heated to 180 °C and the pressure was reduced gradually to 400 Pa in about 40 min. The reaction was continued at 180 °C/400 Pa for 10 h.

2.4. Aftertreatments and characterization of nanocomposites

A repeated dispersion/centrifugation process was used to separate the OLLA-grafted SiO_2 nanoparticles (*g*-SiO_2) from the poly(L-lactic acid) (PLLA) matrix. The PLLA/SiO_2 nanocomposite was dissolved/dispersed in chloroform and then centrifugated at 8000 rpm for 15 min. The supernatant solution was precipitated in ether to obtain pure PLLA samples for molecular weight measurement. And for the resulting crude SiO_2 nanoparticles, the dispersion/centrifugation operation was performed repeatedly for 5–6 times until no absorption of lactate moiety could be detected by FTIR in the supernatant. After drying under vacuum at 60 °C for over 24 h to remove the residual chloroform, the separated *g*-SiO_2 was characterized with TGA and FTIR.

An erosion process was used to cut the grafted OLLA chain (*g*-OLLA) from the centrifugation-separated *g*-SiO_2 particles. The *g*-SiO_2 sample was dispersed in pyridine, and then the dispersion was poured into excessive HF aqueous solution (40%). The SiO_2 was eroded by HF and eliminated in a few minutes, and the residual *g*-OLLA was precipitated and separated by centrifugation. After drying at 60 °C and under vacuum for over 24 h, the molecular weight of *g*-OLLA was determined by GPC.

The molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC, Waters Alliance GPCV 2000) equipped with a refractive index detector. The measurement was performed at 30 °C an at a flow rate of 1 mL/min using chloroform as eluent. The molecular weight was calibrated according to polystyrene standards (Polyscience Co.).

Fourier Transform Infrared spectrometry (FTIR, Nicolet 5700) was employed to characterize the pure PLLA, pure SiO_2 nanoparticle (*p*-SiO_2), *g*-SiO_2 and physically treated SiO_2 nanoparticles (*a*-SiO_2, see Section 3). All the samples were mixed with KBr powders and pressed into a disk for the measurement.

Thermogravimetric Analysis (TGA, Perkin–Elmer Pyris 1) was performed for the samples of pure PLLA, *p*-SiO_2, *g*-SiO_2 and the PLLA/SiO_2 nanocomposites to quantitatively determine the grafting ratio and efficiency as well as the thermal stability. The measurement was performed under nitrogen atmosphere and the heating rate was 20 °C/min.

Transmission Electron Microscope (TEM, JEM-1230) was used to observe the dispersivity of SiO_2 nanoparticles in LLA monomer, OLLA and PLLA matrix. To monitor the dispersivity during dehydration/oligomerization, the TEM specimens were prepared by dipping the TEM coppery grid covered with a

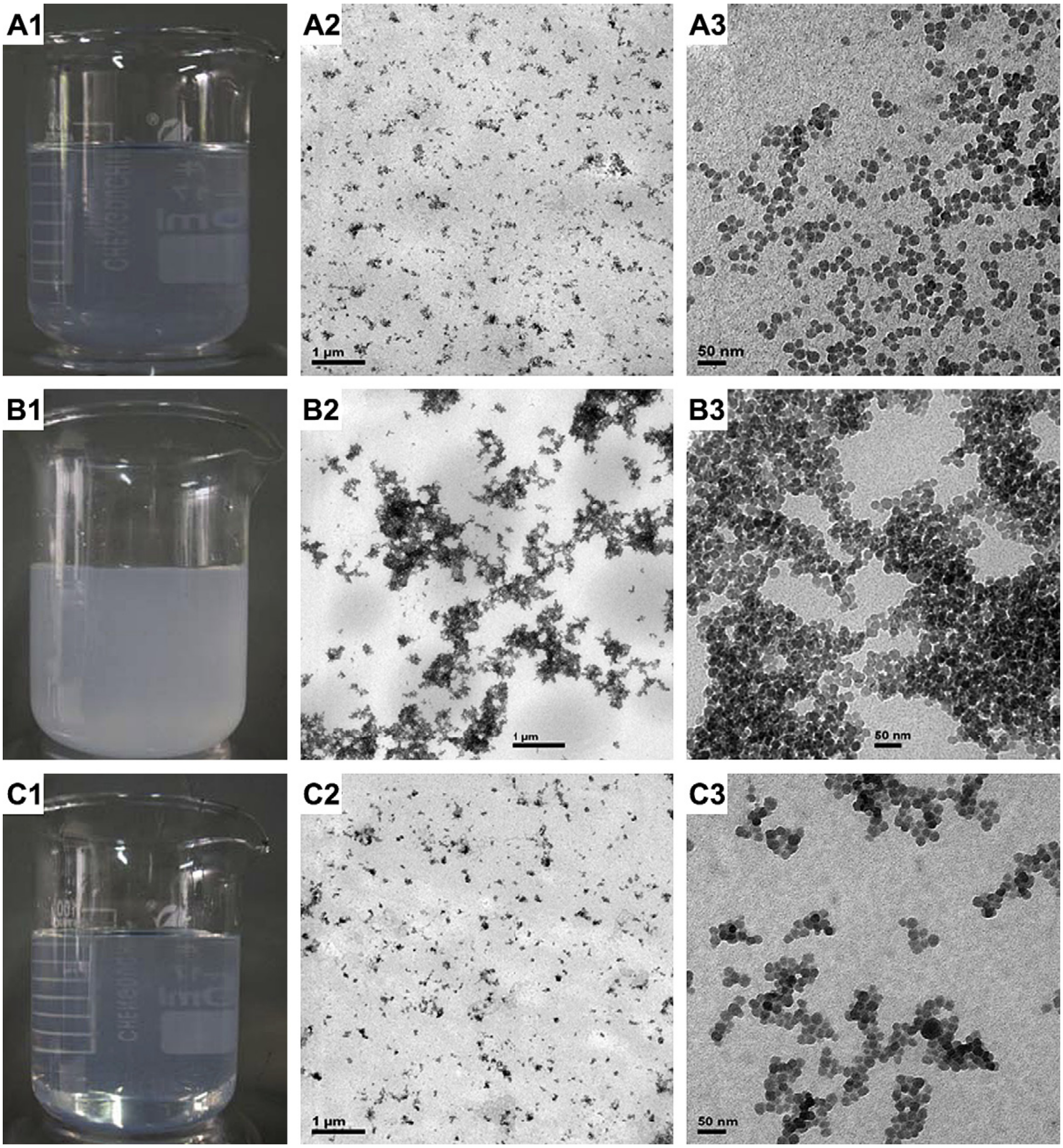

Fig. 1. The appearances (A1–C1) and TEM micrographs (A2–C2 and A3–C3) of the reaction mixture of LLA/aSS during the dehydration/oligomerization process (Run 6, Table 1). (A) After the first ultrasonic treatment; (B) after reaction for 2 h; (C) after the second ultrasonic treatment.

formvar film into the liquid reaction mixture and evaporating the water completely under vacuum. For observation of the dispersivity in the nanocomposites, the TEM specimens were prepared by ultrathin sectioning. The ultrathin section (about 80 nm) was supported by a TEM coppery grid for TEM observation.

Light transmittance of films of pure PLLA and nanocomposites was measured using an ultraviolet–visible light spectrophotometer (UV-3150) over a range of wavelength λ from 390 nm to 770 nm to investigate the effect of nanoparticles on the transparency of the nanocomposites. The films were all amorphous and prepared by spin coating, melting and then quenching in liquid nitrogen. The thickness was of 200 ± 20 µm.

3. Results and discussion

3.1. Dispersion and surface grafting of SiO_2 nanoparticles

The acidic silica sol used in this work is an aqueous dispersion system of SiO_2 nanoparticles in water, with a pH value of about 2.5. It appears as a transparent solution with blue light. It is kinetically stable at acidic environment due to the existence of electrical double layers around the nanoparticles. When it was directly mixed with a colorless and transparent LLA aqueous solution ($pH = 3$), a transparent dispersion with blue light was obtained. After ultrasonic treatment for 30 min, its appearance (Fig. 1(A1)) remained unchanged.

The TEM micrographs (Fig. 1(A2,A3)) indicate that the SiO_2 nanoparticles were dispersed well in the LLA solution, suggesting that the stable double electrode layers remained almost unchanged.

The nanoparticles retained stability in the initial stage of dehydration/oligomerization. But the reaction mixture became turbid after about 2 h (Fig. 1(B1)) and partial aggregation was observed (Fig. 1(B2,B3)). Fortunately, the aggregated nanoparticles could be re-dispersed by a second ultrasonic treatment and the reaction mixture got transparent again (Fig. 1(C)). The nanoparticles remained stably dispersed and the reaction mixture remained transparent during the dehydration/oligomerization process thereafter. A viscous transparent liquid (semi-solid at room temperature) of OLLA/SiO_2 was obtained after oligomerization for 9 h.

During the dehydration/oligomerization process, several reactions took place simultaneously. The condensation among LLA and its oligomer (OLLA) took place in the matrix and led to chain growth. The condensation between the silanol group and LLA and OLLA occurred on the nanoparticle surfaces and resulted in grafting of LLA and OLLA onto the nanoparticles. The grafted OLLA chain provided extra steric stabilization for the nanoparticles. However, when free water was almost removed, the charge state on the particle surfaces was changed and the electrical double layers partially destroyed. Therefore, the stability of the nanoparticles was weakened and aggregation took place. But the aggregation was incompact due to grafting and therefore easily broken again by ultrasonic treatment. The nanoparticles were thus re-dispersed in the matrix.

At the initial stage of dehydration/oligomerization, the starting LLA, its primary condensates (a few units) and the surface of fresh SiO_2 nanoparticles are all of high polarity. The polarity of the reaction matrix was greatly reduced with chain growth and dehydration since the OLLA contains less carboxyl and hydroxyl groups than the LLA monomer [27]. Similar polarity change occurred on the surface of the nanoparticles due to grafting. Such synchronous changes of polarity in the matrix and on the surfaces and the increasing steric stabilization resulted in the fact that the nanoparticles got stable and most aggregates disappeared after the second ultrasonic treatment.

During the succedent melt polycondensation process, the SiO_2 nanoparticles still remained stably dispersed due to continuous grafting. Fig. 2 shows the TEM micrographs of the resulting PLLA/SiO_2 nanocomposites. The nanoparticles were clearly densified with increasing SiO_2 content ($\phi_{\mathrm{Si,c}}$) from 5.0% to 19.1% and well dispersed in nano-scale in the PLLA matrix. Because of the enhanced steric stabilization during melt polycondensation, better dispersivity (Fig. 2(C)) was observed as compared with the case after the second ultrasonic treatment (Fig. 1(C3)). A little of aggregation is still observed, but is slight and incompact. And its dimension is less than 100 nm such that they do not clearly affect the transmittance of the nanocomposite films, as shown in Table 1. To exclude the effect of crystallization, amorphous samples were prepared for light transmittance measurement. In the visible light range (390–770 nm), the transmittance of the nanocomposite films is comparable to that of pure PLLA film. The transmittance of all the samples lies in the range of 96–99% and slightly increased when the wavelength shifted from 390 nm to 770 nm.

Therefore, a satisfactory nano-scale dispersion of SiO_2 nanoparticles in PLLA matrix was accomplished with the in situ melt polycondensation of LLA/aSS presented here. It should be noted that incorporation of 5% or less of nanoparticles is often enough for nanocomposites. The purpose of using silica nanoparticles over 19% is to demonstrate dispersion ability of this method. In addition, PLLA nanocomposites with high amount of silica nanoparticles may also be used as nano masterbatch for blending with pure PLLA or other biodegradable polymers.

In addition to the nano-scale uniform dispersion, interfacial interaction is another important factor for a nanocomposite. In general, chemical grafting of polymer chains which are compatible to the polymer matrix on the inorganic particles provides strong interfacial interaction between the inorganic and organic phases [28]. The existence of the silanol group on the surface of SiO_2 and the carboxyl group in LLA and OLLA provides a possibility of grafting LLA and OLLA onto the surface of SiO_2. The FTIR analysis validated qualitatively the grafting reaction. Fig. 3 illustrates the FTIR spectra of pure SiO_2 particles (A, p-SiO_2), SiO_2 particles separated from the nanocomposite via repeated dispersion/centrifugation (B, g-SiO_2) and pure PLLA (C). Compared to p-SiO_2, new absorption bands appear at 1759 cm^{-1}, 2947 cm^{-1} and 2997 cm^{-1} in the spectrum of g-SiO_2. These peaks are attributed to the carbonyl group (C=O), methine and methyl of the OLLA grafted on the g-SiO_2 nanoparticles (g-OLLA), respectively. In order to exclude the possibility that PLLA physically adsorbed onto the surface of SiO_2, a control sample (a-SiO_2) was prepared by mixing 0.5 g of pure SiO_2 nanoparticles with a chloroform solution of PLLA, stirring for 10 h and then repeating the centrifugation/re-dispersion cycles, and characterized by FTIR likewise. It is clear that its FTIR spectrum (Fig. 3D) is in accordance with that of p-SiO_2 and no characteristic peak of lactate moiety was observed. These results confirm that OLLA was chemically grafted onto SiO_2 surface.

The thermogravimetric analysis (TGA) further provided quantitative evidence of grafting. Fig. 4 shows four typical TGA curves. The pure SiO_2 (A) is thermally stable at temperature higher than 800 °C, but the pure PLLA (D) thermally degraded at temperature higher than 300 °C. The difference ($W_{g\text{-OLLA}}^{g\text{-SiO}_2}$) between the residual weight of g-SiO_2 (sample B) and that of p-SiO_2 (sample A) represents the content of g-OLLA in g-SiO_2 and $(1 - W_{g\text{-OLLA}}^{g\text{-SiO}_2})$ represents the net weight of SiO_2 nanoparticles, see Fig. 4. So the grafting ratio (G_r) is defined by Eq. (1). The difference ($W_{\text{PLLA}+g\text{-OLLA}}^{\text{comps}}$) between the residual weight of the PLLA/SiO_2 nanocomposite (sample C) and that of p-SiO_2 (sample A) represents the total weight of PLLA matrix and g-OLLA, see Fig. 4. As a result, $(1 - W_{\text{PLLA}+g\text{-OLLA}}^{\text{comps}})$ represents the fraction of SiO_2 in the nanocomposite, $\phi_{\mathrm{Si,c}}$. The grafting efficiency (G_e) can be calculated using Eq. (3). The results are listed in Table 1.

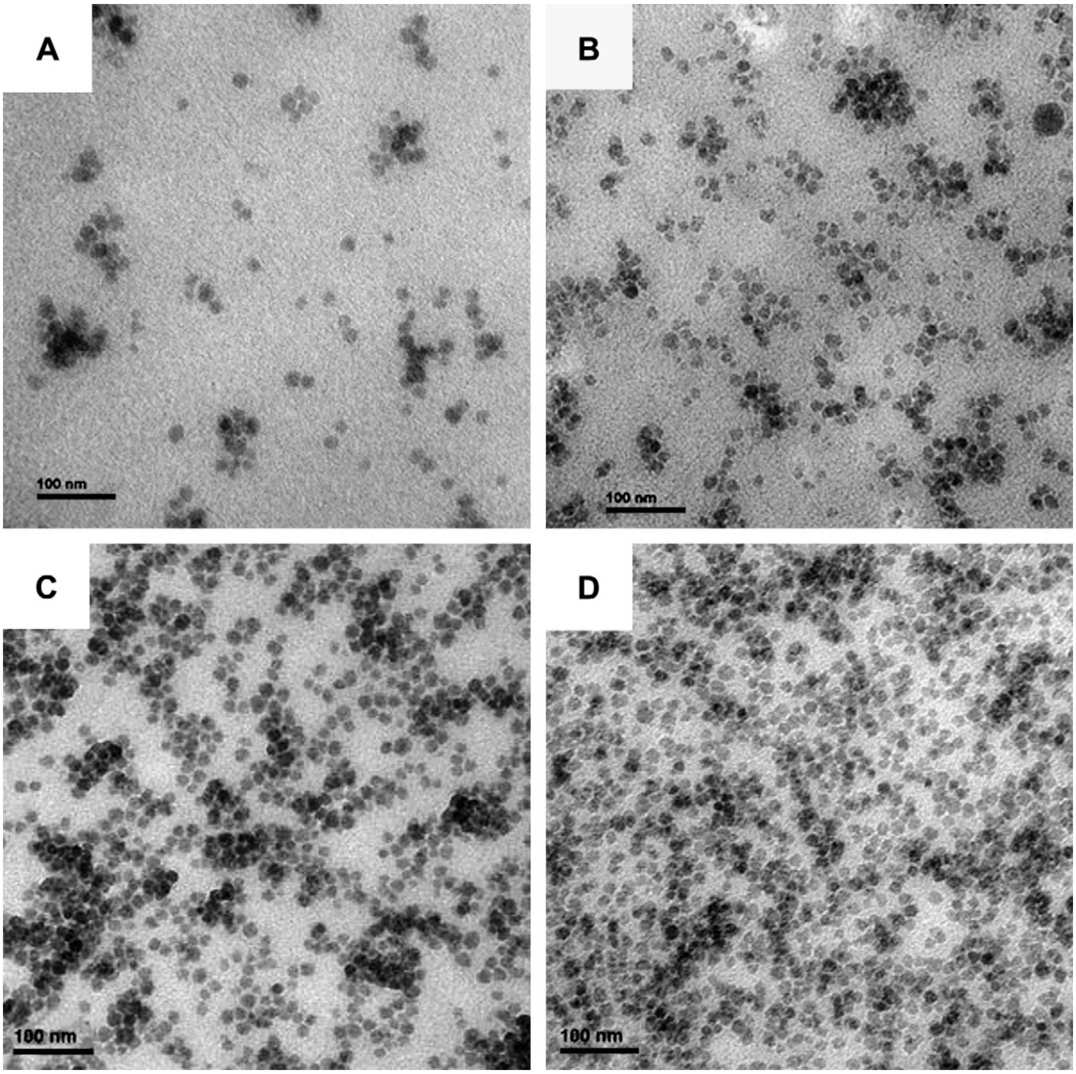

Fig. 2. TEM micrographs of PLLA/SiO$_2$ nanocomposites with various SiO$_2$ contents, $\phi_{\mathrm{Si,c}}$: (A) 5.0 wt%; (B) 7.6 wt%; (C) 10.5 wt%; (D) 19.1 wt%.

$$G_\mathrm{r} = \frac{W_{g\text{-OLLA}}^{g\text{-SiO}_2}}{1 - W_{g\text{-OLLA}}^{g\text{-SiO}_2}} \tag{1}$$

$$\phi_{\mathrm{Si,c}} = 1 - W_{\mathrm{PLLA}+g\text{-OLLA}}^{\mathrm{comps}} \tag{2}$$

$$G_\mathrm{e} = \frac{\phi_{\mathrm{Si,c}} G_\mathrm{r}}{W_{\mathrm{PLLA}+g\text{-OLLA}}^{\mathrm{comps}}} \tag{3}$$

As expected, the grafting ratio decreased, but the grafting efficiency increased with increasing SiO$_2$ content. The grafting ratio was higher than 40%, and the grafting efficiency lies in the range of 2.8–8.0%, see Table 1. The TGA results also indicate the effect of incorporation of SiO$_2$ nanoparticles on the thermal stability. The decomposition temperature at 5% weight loss ($T_{\mathrm{d,5}}$) started to increase when more than 5 wt% SiO$_2$ was incorporated. It was raised by 20 °C (from 232 °C to 252 °C) at $\phi_{\mathrm{Si,c}}$ of 19.1 wt%.

A *g*-SiO$_2$ sample separated from sample Run 7 was further eroded with HF to cut down the *g*-OLLA chains for molecular weight measurement. TGA of the resultant *g*-OLLA revealed that the SiO$_2$ was removed completely by erosion and a control experiment confirmed that the erosion did not obviously affect the molecular weight (less than 10% decrease). The GPC measurement indicated that the grafting OLLA has a peak molecular weight of about 31 100, being smaller than that of the matrix.

From the above results, it is concluded that OLLA was chemically grafted onto the surface of the SiO$_2$ nanoparticles.

3.2. *Effect of SiO$_2$ on the melt polycondensation*

The yield and molecular weight of the PLLA matrix are important quantities to be concerned. High molecular weight is essential for satisfactory mechanical properties. The effect of SiO$_2$ on the yield and molecular weight of PLLA matrix is shown in Table 1.

The yield remained unchanged (88–91%) in the experimental range examined. The molecular weight also kept almost constant at $\phi_{\mathrm{Si,c}}$, not more than 7.6 wt%, but decreased when

Table 1

In situ melt polycondensation of LLA/aSS using $SnCl_2 \cdot 2H_2O$/TSA as catalyst (180 °C, 400 Pa, 10 h)

Run	$\phi_{Si,c}$[a] (%)	y[b] (%)	$M_{w,PLLA}$[c]	M_w/M_n[c]	G_r[d] (%)	G_e[e] (%)	φ_{tr}[f] (%)	$T_{d,5}$ (°C)	$T_{d,max}$ (°C)	Color[g]
1	0	88.6	102 000	1.5	–	–	96.8–99.1	232	298	LY
2	3.5	88.8	119 400	1.4	nd	nd	nd	233	288	SY
3	5.0	88.1	109 900	1.4	nd	nd	96.1–98.9	233	284	SY
4	6.1	87.4	nd	nd	60.0	2.8	nd	237	295	SY
5	7.6	89.1	90 600	1.4	49.5	3.1	nd	241	302	W
6	10.5	90.2	76 300	1.3	48.1	4.2	nd	245	304	W
7	19.1	90.7	57 400	1.3	44.3	8.0	97.7–97.8	252	310	W

[a] SiO_2 content in the nanocomposite.
[b] Yield of PLLA.
[c] Weight average molecular weight of the PLLA matrix.
[d] Grafting ratio.
[e] Grafting efficiency.
[f] Light transmittance of amorphous films of PLLA and its nanocomposites.
[g] LY: light yellow; SY: slight yellow; W: white.

more SiO_2 was introduced. Under same polycondensation conditions, the weight average molecular weight decreased by 11%, 25% and 44% as compared with pure PLLA when 7.6 wt%, 10.5 wt% and 19.1 wt% SiO_2 was introduced. Two possible reasons are responsible for the reduction of molecular weight. First, the presence of extra silanol groups on the SiO_2 particles broke the intrinsic balance of carboxyl and hydroxyl (COOH/OH 1:1) in LLA, and therefore reduced the theoretical molecular weight at a complete conversion of COOH. Second, as compared with PLLA with same molecular weight, it was observed that the nanocomposite melts with high SiO_2 content had higher viscosity, which depressed diffusion of water and therefore the growth of the molecular weight.

Discoloration is usually a headache in melt polycondensation of LLA [27]. In despite of the disadvantageous effect on the molecular weight growth at high $\phi_{Si,c}$, the presence of SiO_2 nanoparticles appears to be conducive to depress discoloration. Melt polycondensation of LLA alone for 10 h resulted in light yellowish PLLA. Introduction of 3.5–6.1 wt% SiO_2 produced slight yellow nanocomposites, and introduction of SiO_2 higher than 7.6 wt% produces nearly white nanocomposites, as seen in Table 1.

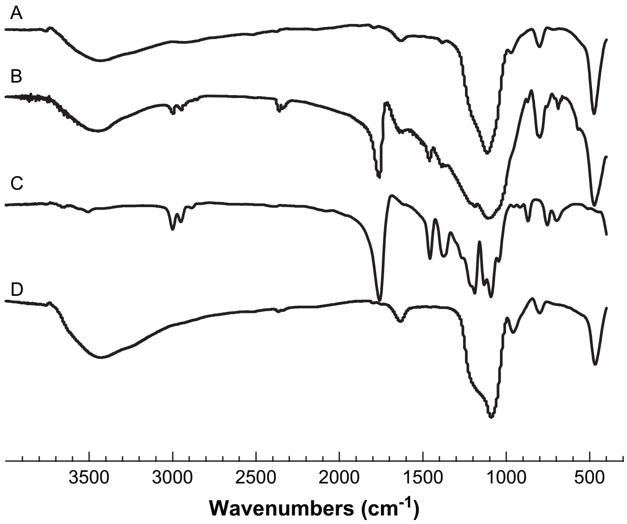

Fig. 3. FTIR spectra of (A) *p*-SiO_2 (pure SiO_2 nanoparticles), (B) *g*-SiO_2 (SiO_2 nanoparticles grafted with OLLA), (C) pure PLLA and (D) *a*-SiO_2 (a comparative sample physically treated, see text).

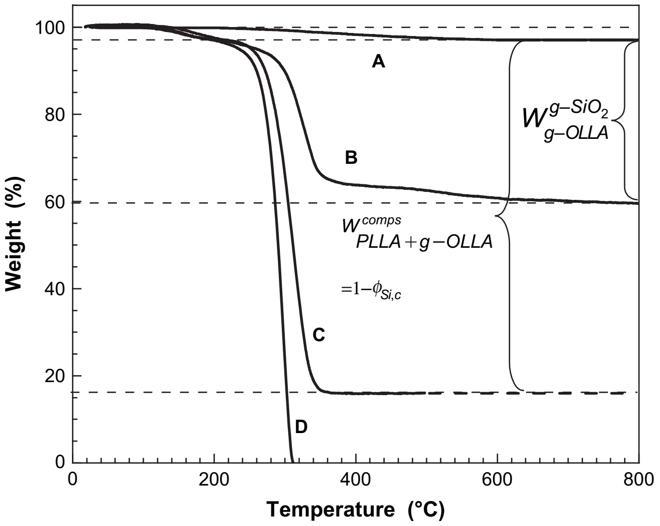

Fig. 4. TGA curves of (A) *p*-SiO_2, (B) *g*-SiO_2, (C) PLLA/SiO_2 nanocomposite (Run 7, Table 1) and (D) pure PLLA.

4. Conclusions

In situ melt polycondensation of L-lactic acid in the presence of acidic silica sol (aSS) has been proposed for the first time to prepare PLLA/SiO_2 nanocomposites. The stability of aSS under acid and polar aqueous environment ensured easy dispersion of SiO_2 nanoparticles in the LLA monomer. During the polycondensation process, chain growth occurred in the PLLA matrix and chemical grafting took place on the SiO_2 surface so that the matrix and SiO_2 surface changed nearly synchronously from high polarity/hydrophilicity to weak polarity/hydrophobicity. Incompact aggregation took place in the dehydration/oligomerization process, but the aggregates were readily redispersed with the aid of ultrasonic due to steric stabilization resulted from the surface grafting. Therefore, in the resulting nanocomposites, the SiO_2 nanoparticles were chemically grafted with OLLA chains and well dispersed on nano-scale in the PLLA matrix. The grafting ratio and efficiency reached

44–60% and 2.8–8.0%, respectively. The presence of SiO_2 nanoparticles resulted in unchanged yield and better color. The molecular weight remains almost unchanged at SiO_2 content not more than 7.6 wt%.

In addition to satisfactory dispersion and surface grafting, this method is also characterized by commercially available and cheap starting materials and environmentally benign process. These advantages make it appear a promising approach for the preparation of PLLA/SiO_2 nanocomposites. Our efforts to examine the mechanical properties are under way.

Acknowledgements

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References

[1] Drumright RE, Gruber PR, Henton DE. Adv Mater 2000;12:1841–6.
[2] Sodergard A, Stolt M. Prog Polym Sci 2002;27:1123–63.
[3] Bendix D. Polym Degrad Stab 1998;59:129–35.
[4] Kovalchuk A, Fischer W, Epple M. Macromol Biosci 2005;5:289–98.
[5] Paul M-A, Alexandre M, Degee P, Henrist C, Rulmont A, Dubois P. Polymer 2003;44:443–50.
[6] Kasuga T, Ota Y, Nogami M, Abe Y. Biomaterials 2001;22:19–23.
[7] Zhang DH, Kandadai MA, Cech J, Roth S, Curran SA. J Phys Chem B 2006;110:12910–5.
[8] Yan SF, Yin JB, Yang Y, Dai ZZ, Ma J, Chen XS. Polymer 2007;48:1688–94.
[9] Ray SS, Bousmina M. Prog Mater Sci 2005;50:962–1079.
[10] Ray SS, Maiti P, Okamoto M, Yamada K, Ueda K. Macromolecules 2002;35:3104–10.
[11] Chen GX, Kim HS, Shim JH, Yoon JS. Macromolecules 2005;38: 3738–44.
[12] Paul M-A, Alexandre M, Degée P, Calberg C, Jérôme R, Dubois P. Macromol Rapid Commun 2003;24:561–6.
[13] Paul M-A, Delcourt C, Alexandre M, Degée P, Monteverde F, Rulmont A, et al. Macromol Chem Phys 2005;206:484–98.
[14] Joubert M, Delaite C, Bourgeat-Lami E, Dumas P. J Polym Sci Part A Polym Chem 2004;42:1976–84.
[15] Bourgeat-Lami E, Lang J. J Colloid Interf Sci 1998;197:293–308.
[16] Liu YL, Chin YH, Chen HS. Nanotechnology 2003;14:813–9.
[17] Ding XF, Jiang YQ, Yu KF, Hari-Bala, Tao NN, Zhao JZ, et al. Mater Lett 2004;58:1722–5.
[18] Perry CC, Eglin E, Ali SAM, Downes S. Mater Res Soc Symp Proc 2002;726:67–78.
[19] Sengupta R, Bandyopadhyay A, Sabharwal S, Chaki TK, Bhowmick AK. Polymer 2005;46:3343–54.
[20] Wen Y, Yang DC, Tang LG, Hutchins MK. J Mater Res 1993;8:1143–7.
[21] Pope EJA, Sami MA, Mackenzie JD. J Mater Res 1989;4:1018–25.
[22] Patel S, Bandyopadhyay A, Vijayabaskar V, Bhowmick AK. Polymer 2005;46:8079–90.
[23] Jain S, Goossens H, Picchioni F, Magusin P, Mezari B, van Duin M. Polymer 2005;46:6666–81.
[24] Yoon KR, Lee Y-W, Lee JK, Choi IS. Macromol Rapid Commun 2004;25:1510–3.
[25] Han MG, Armes SP. J Colloid Interf Sci 2003;262:418–27.
[26] Amalvy JI, Percy MJ, Armes SP. Langmuir 2005;21:1175–9.
[27] Moon SI, Lee CW, Miyamoto M, Kimura Y. J Polym Sci Part A Polym Chem 2000;38:1673–9.
[28] Hong ZK, Zhang PB, He CL, Qiu XY, Liu AX, Chen L, et al. Biomaterials 2005;26:6296–304.