ORIGINAL PAPER

Preparation and thermo-oxidative degradation of poly(L-lactic acid)/poly(L-lactic acid)-grafted SiO$_2$ nanocomposites

Deling Li · Guangtian Liu · Lihong Wang · Yulong Shen

Abstract Poly(L-lactic acid)/poly(L-lactic acid)-grafted SiO$_2$ nanocomposites were prepared by in situ melt polycondensation, in which "free" poly(L-lactic acid) and poly(L-lactic acid)-grafted SiO$_2$ nanoparticles were formed simultaneously. The maximum values of grafting ratio and grafting efficiency of poly(L-lactic acid) were up to 37.67% and 26.60%, respectively. In the polycondensation system, SiO$_2$ content was a critical parameter of getting nanocomposites with uniformly dispersed SiO$_2$ nanoparticles. At lower SiO$_2$ content, Mn of grafted poly(L-lactic acid) was close to that of "free" poly(L-lactic acid), and poly(L-lactic acid)-grafted SiO$_2$ nanoparticles could be well dispersed in poly(L-lactic acid) matrix. While at higher SiO$_2$ content, Mn of "free" poly(L-lactic acid) and grafted poly(L-lactic acid) decreased seriously, especially GPC curves of "free" poly(L-lactic acid) exhibited two peaks due to the aggregation of SiO$_2$ nanoparticles during the polycondensation process. The grafting ratio and SiO$_2$ content exhibited a clear effect on the thermo-oxidative degradation of nanocomposites. The existence of poly(L-lactic acid)-grafted SiO$_2$ nanoparticles dramatically improved the thermo-oxidative stability of poly(L-lactic acid). Compared with that of pure poly(L-lactic acid), T_g, T_c, and T_m of nanocomposites varied slightly.

D. Li (✉) · L. Wang · Y. Shen
Department of Chemistry, Tangshan Normal University,
Tangshan 063000, China
e-mail: delingshi@sina.com.cn

G. Liu
College of Environmental and Chemical Engineering, Yanshan University,
Qinhuangdao 066004, China

Introduction

Poly(L-lactic acid) (PLLA) has been accepted as an ideal alternative to the current
packing materials based on fossil fuel, such as polyethylene (PE) and polypropylene
(PP) [1, 2], not only because of its good mechanical properties that are comparable
to PE and PP, but also because of its excellent environmental suitability. In recent
years, considerable attentions have been paid to PLLA matrix organic–inorganic
composites [3–7] as they could exhibit desirable physical and chemical properties.
However, inorganic nanoparticles are easy to aggregate and difficult to be dispersed
uniformly in PLLA matrix due to their insolubility and the inherently poor
compatibility between nanoparticles and polymers, resulting in inhomogeneous
composites with unsatisfying properties. In order to prevent the aggregation, then to
get uniformly dispersed inorganic particles in PLLA matrix, and thus to achieve
nano-scale organic–inorganic composites, the effective modification of inorganic
particles is necessary [8, 9]. Wu and Liao [10] reported the preparation of PLLA/
multi-walled carbon nanotubes composites, in which multi-walled carbon nanotubes
was pretreated with 1,6-hexanediol. Nakayama and Hayashi [11] also pretreated the
surface of TiO_2 particles with propionic acid or *n*-hexylamine, and subsequently
prepared PLLA/TiO_2 composites with the enhanced compatibility between PLLA
and TiO_2. The application of acidic silica sol in PLLA using in situ melt
polymerization was reported by Wu et al. [12, 13]. The distribution of silica in the
according nanocomposites reached nano-scale because of the grafted PLLA chain
from the silica surface. In Wu's polycondensation system, acidic water solution
would help the stable dispersion of SiO_2 in the polymerization solution. But lots of
time would be involved to remove large amount of water from the polycondensation
system in the latter stage. Especially, the removal of such large amount of water at a
time would lead to the serious aggregation of SiO_2, which involved a second
sonication in the polycondensation process.

   SiO_2 powder, as a cheap starting nanomaterial, could be widely applied into
nanomaterial industry [14, 15]. Compared with acidic silica sol, SiO_2 powder is
much cheaper and more convenient for storage and transportation because of its
excellent stability. Therefore, the application of SiO_2 powder in PLLA is more
suitable for the development of industry. In this paper, SiO_2 powder was directly
dispersed in 85% LLA by sonication, subsequently in situ melt polymerization
was conducted to prepare PLLA/PLLA-grafted SiO_2 nanocomposites. The effect
of SiO_2 content on polycondensation process was discussed. There have been
relatively few publications on the thermo-oxidative stability of PLLA/PLLA-
grafted SiO_2 nanocomposites, which would be of crucial importance for practical
applications. Thus, the thermo-oxidative degradation of PLLA/PLLA-grafted
SiO_2 nanocomposites with various SiO_2 content was also investigated in our
work.

Experimental

Materials

SiO_2 powder used was Aerosil 200 (Degussa) with a specific surface area of 200 ± 25 m^2 g^{-1}. L-Lactic acid (LLA) as a 85 wt% aqueous solution was purchased from Tianjin Guangfu Fine Chemical Research Institute. Tin(II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$), p-toluenesulfonic acid monodrate (TSA) were purchased from Tianjin Damao Chemical Reagent Factory. Other chemical reagents were also obtained from Tianjin. All these materials were used without further purification.

Preparation of PLLA/PLLA-SiO_2 nanocomposites

The procedure of run **1** is typical. 0.8 g of SiO_2 powder was mixed with 80 mL LLA and sonicated for 30 min, leading to a suspension. The suspension was immediately transferred to a 250 mL three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a vacuum system. The mixture was first dehydrated for 2 h at 150 °C and 3000 Pa. Then, $SnCl_2 \cdot 2H_2O$ (0.2 wt% relative to LLA) and TSA (an equimolar ratio to $SnCl_2 \cdot 2H_2O$) were added into the flask. The reaction system was heated to 180 °C under mechanical stirring and its pressure was reduced stepwise to 2000 Pa in 1 h, at which pressure the reaction continued for 10 h. In this reaction, L-lactide was refluxed through the hot reflux condenser. The product was then dissolved in 500 mL trichloromethane, forming a transparent solution. An aliquot of the solution was then taken out and precipitated with diethyl ether. The resulted white power was PLLA/PLLA-grafted SiO_2 nanocomposites. The rest of the solution was centrifuged at 8000 min^{-1} for 30 min. The supernatant solution, which contained "free" PLLA formed in bulk, was decanted, then poured into excess diethyl ether and filtered off. The solid remained after decanting was then further dissolved in trichloromethane, ultrasonicated for 30 min at room temperature and centrifuged. In order to obtain PLLA-grafted SiO_2 perfectly "free" of the nonbonded PLLA, this cycle of dispersion–centrifugation in trichloromethane was conducted until no more precipitate formed when the supernatant liquid was added dropwise to the methanol. PLLA/PLLA-grafted SiO_2 nanocomposites, "free" PLLA and PLLA-grafted SiO_2 were dried in a fume hood and then in a vacuum oven at room temperature.

Runs **2**, **3**, **4**, and **5** were performed at the same procedure with the above except that the weight of SiO_2 powder was 2, 4, 8, and 12 g, respectively.

General procedures for cleaving grafted PLLA from SiO_2 powder

In order to get the information of grafted PLLA, grafted PLLA was cleaved off from the surfaces of SiO_2 powder.

300 mg of PLLA-grafted SiO_2 was dispersed in 100 mL trichloromethane, to which a 40% HF aqueous solution (10 mL) was added. The mixture was vigorously stirred for 24 h at −5 °C. The organic phase was concentrated into 5 mL, poured

into 100 mL dithyl ether and filtered off. The cleaved PLLA, namely grafted PLLA, was dried in a fume hood and then in a vacuum oven at room temperature.

Characterization

All tested samples were dried under vacuum at 60 °C for 24 h before use.

The Fourier transform absorption spectra were recorded on a Brucker Tensor 37 FT-IR spectrometer using KBr pellet method.

Thermal gravimetric analysis (TGA) was conducted on a Perkin-Elmer Pyris 1 thermal gravimetric analyser. Samples were heated from 30 to 800 °C at the heating rate of 10 °C min^{-1}. The air flow rate was kept at 60 mL min^{-1}.

Differential scanning calorimetry (DSC) was conducted on a Perkin-Elmer DSC system under N$_2$ atmosphere. The sample was first heated from 30 to 200 °C at 10 °C min^{-1} and maintained at 200 °C for 3 min, then cooled to −30 °C at −100 °C min^{-1} and maintained at −30 °C for 3 min, and finally heated at 10 °C min^{-1} from −30 °C to 200 °C.

The molecular weight of "free" PLLA and grafted PLLA were determined by a gel permeation chromatography (GPC), Water 1525/2424/2487 system. Three linear PL Waters Styragel Columns (HR2, HR3 and HR4) were used. The eluent was THF with a flow rate of 1 mL min^{-1} at 30 °C. The data were calibrated with polystyrene standards with molecular weights ranging from 980 to 710,000 g mol^{-1}.

TEM observation was made on a JEOL JEM-2010 transmission electron microscope at an acceleration voltage of 200 kV.

Results and discussion

Surface grafting of SiO$_2$ nanoparticles and characterization

In this paper, SiO$_2$ powder was directly dispersed in LLA by sonication, and then PLLA/PLLA-grafted SiO$_2$ nanocomposites were prepared by in situ melt polymerization. Compared with the system reported by Wu [12, 13], our polycondensation process was much simpler due to the less time consuming and the avoided second sonication. The whole procedure of polycondensation and treatments of products are shown in Scheme 1. The polycondensation of LLA proceeded in bulk and the surfaces of SiO$_2$ simultaneously. It is reported that the number of silanol groups on SiO$_2$ is 4–5 SiOH/nm^2 [16, 17]. The high local concentration of silanol group on SiO$_2$, together with its uniform distribution in polymerization system, led to the condensation reaction of silanol groups with LLA, subsequently the propagation of grafted chains from the surface of silica particles. The resulted products were PLLA/PLLA-grafted SiO$_2$ nanocomposites, which consisted of PLLA-grafted SiO$_2$ deriving from the polymerization from the silica surface and "free" PLLA deriving from polymerization in bulk.

Figure 1 shows the FT-IR spectra of bare SiO$_2$, PLLA-grafted SiO$_2$, "free" PLLA, and grafted PLLA of the samples of run **1**. The absorption band of 3400 cm^{-1} in Fig. 1b belonged to non-reacted silanol of PLLA-grafted SiO$_2$, which
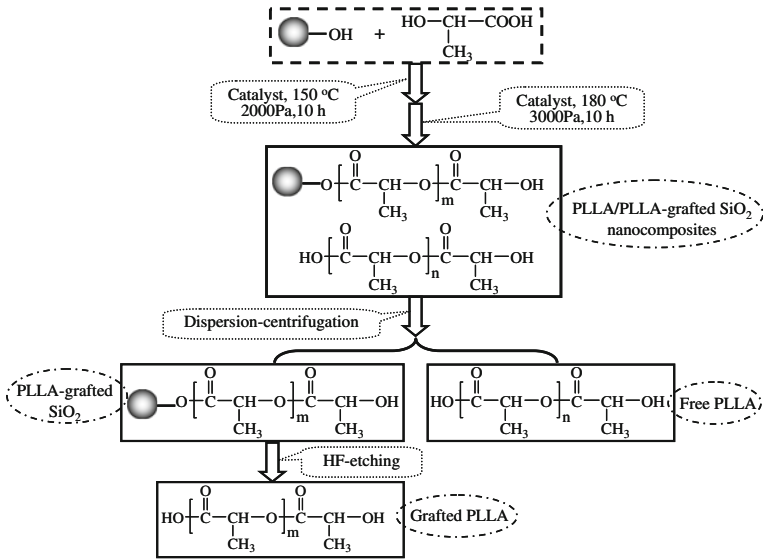
Scheme 1 Schematic illustration of the procedure of polycondensation and treatments of products

Fig. 1 FT-IR spectra of
(*a*) bare SiO_2, (*b*) PLLA-grafted
SiO_2, (*c*) "free" PLLA, and
(*d*) grafted PLLA of the samples
of run **1**
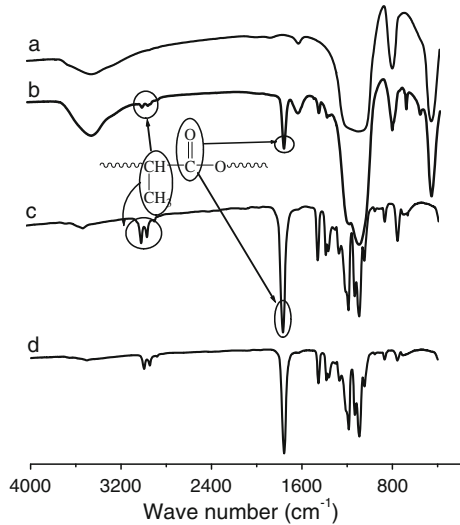
was also existed in Fig. 1a. The absorption bands of 1759.9 cm^{-1} and 2990–2950 cm^{-1} of PLLA-grafted SiO_2 belong to the carbonyl and the C–H stretching vibrations, respectively, which is in good agreement with the spectrum of "free" PLLA. Especially, the spectrum of grafted PLLA is the same with "free" PLLA. The results of other runs are identical with run **1**. These detail analysis qualitatively illustrated that the polycondensation of LLA did happen on the surfaces of silica particles.

Fig. 2 TG curves of (*a*) bare SiO₂, (*b*) PLLA-grafted SiO₂, (*c*) PLLA/PLLA-grafted SiO₂ nanocomposites, and (*d*) "free" PLLA of run **1**
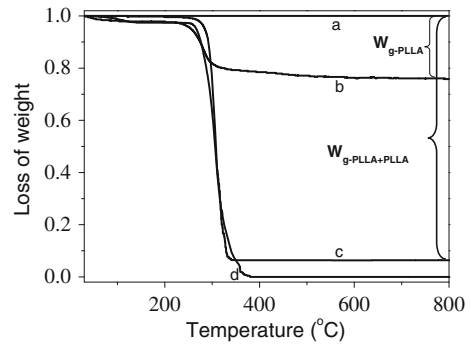
Table 1 Characteristic result of PLLA/PLLA-grafted SiO₂ nanocomposites prepared by in situ melt polycondensation

Run	SiO₂ content (%)	G_r (%)	G_e (%)	Mn of "free" PLLA		Mn of grafted PLLA
1	0.97	31.38	22.90	13017	–	11084
2	2.40	33.60	25.70	12743	–	11487
3	4.70	37.67	26.60	7346	–	5857
4	8.90	31.94	26.50	3426	8987	5145
5	12.80	25.31	25.40	3289	8833	3807

The effect of SiO₂ content on the polycondensation process

The simple way to quantify the grafting ratio is thermal gravimetric analysis [18]. Figure 2 is the TGA traces of bare SiO₂, PLLA-grafted SiO₂, PLLA/PLLA-grafted SiO₂ nanocomposites, and "free" PLLA of run **1**. The weight of bare SiO₂ is kept stable up to 800 °C except that 3% of weight loss due to the dehydroxylation of the silica surface at 350–500 °C. The temperature of full decomposition of "free" PLLA was 381 °C. The weight loss of PLLA-grafted SiO₂ included the dehydroxylation of the silica surface and the decomposition of grafted PLLA when the decomposition temperature was up to 800 °C. $W_{g\text{-}PLLA}$, the weight of grafted PLLA, was obtained from the weight loss of bare SiO₂ and PLLA-grafted SiO₂. The weight loss of PLLA/PLLA-grafted SiO₂ nanocomposite involved the dehydroxylation of the silica surface, the decompositions of grafted PLLA and "free" PLLA. $W_{g\text{-}PLLA+PLLA}$, the weight of grafted and "free" PLLA, was obtained from the weight loss of bare SiO₂, PLLA-grafted SiO₂, and PLLA/PLLA-grafted SiO₂ nanocomposite, as shown in Fig. 2. The grafting ratio (G_r) and grafting efficiency (G_e) of PLLA on silica particles can be calculated using Eqs. 1 and 2, respectively. The data were shown in Table 1. The SiO₂ content in polycondensation system had serious effect on grafting ratio and grafting efficiency. The maximum values of grafting ratio and grafting efficiency were up to 37.67% and 26.60% (Run **3**), respectively. Then, the grafting ratio and grafting efficiency decreased with the increasing SiO₂ content. This demonstrated that the aggregation of SiO₂ existed in

the polycondensation process and got more serious with increasing SiO_2 content. Two possible aggregation of SiO_2 might exist in melt polymerization. The first is that SiO_2 powder aggregated in the initial stage and the polycondensation from the surface of SiO_2 was depressed. The second is that the particles of oligomer PLLA-grafted SiO_2 aggregated in the middle stage and water encapsulated in the aggregated particles could not be removed, which inhibited the further propagation of grafted PLLA chains, and subsequently, led to the decreasing amount of grafted PLLA.

$$G_r = \frac{W_{g-PLLA}}{W_{SiO_2}} \qquad (1)$$

$$G_e = \frac{W_{g-PLLA}}{W_{g-PLLA+PLLA}} \qquad (2)$$

Mn of grafted PLLA was close to Mn of "free" PLLA for run **1** and run **2**, as shown in Table 1. While Mn of grafted PLLA and "free" PLLA decreased seriously as the SiO_2 content increased, especially, two peaks of GPC traces were clearly observed in "free" PLLA of runs **4** and **5**, as shown in Fig. 3. Just as discussed above, it was difficult for the oligomer of PLLA encapsulated in the aggregated particles to further propagate due to the residual water in the aggregate. "Free" PLLA included two parts: PLLA with higher Mn formed outside of aggregated particles and PLLA with lower Mn formed in encapsulated particles, which exhibited two peaks in the GPC traces.

The distributions of PLLA-grafted SiO_2 in PLLA/PLLA-grafted SiO_2 nanocomposite of run **1** and run **4** were studied by TEM, as shown in Fig. 4. Compared with that of run **1**, the clustering in the TEM images of run **4** occurred obviously. This suggested that the surface of SiO_2 (run **1**) had bonded longer PLLA chains, which was in accordance with the results of GPC.

Fig. 3 GPC traces of "free" PLLA formed in polycondensation bulk
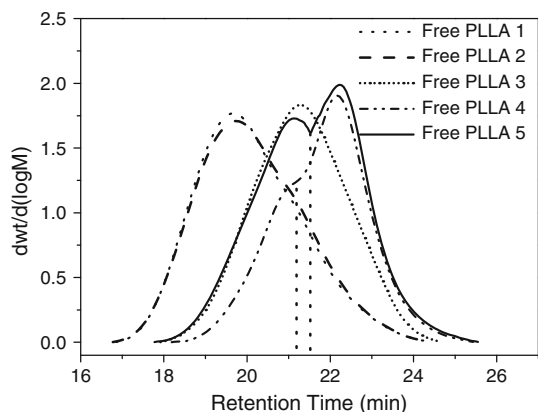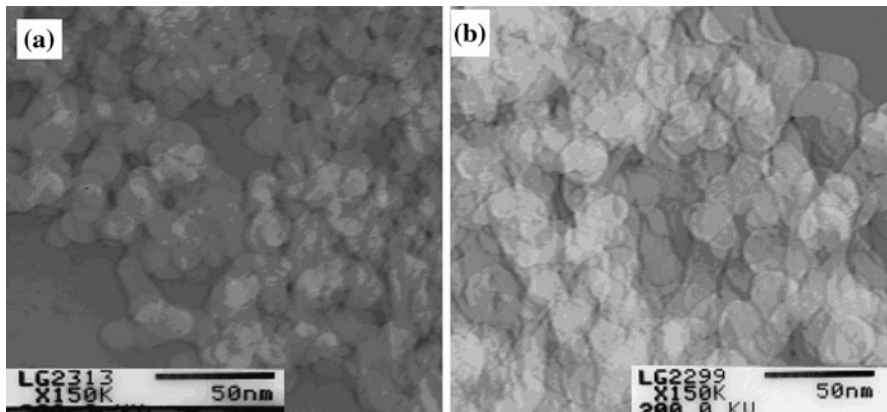
Fig. 4 TEM images of PLLA/PLLA-grafted SiO$_2$ nanocomposite of **a** run **1** and **b** run **4**

Table 2 Thermal properties of PLLA/PLLA-grafted SiO$_2$ nanocomposites

Run	SiO$_2$ content (%)	$T'_{d,0}$	$T'_{d,max}$	T_g	T_c	T_m	$T_{d,0}$	$T_{d,max}$
PLLA[a]	0	–	–	63.45	129.93	149.78	262.29	296.60
1	0.97	245.87	258.63	63.91	129.84	150.20	292.66	312.71
2	2.40	255.68	269.78	63.81	129.12	150.17	293.68	316.05
3	4.70	255.23	294.78	63.80	128.27	149.99	302.09	318.47
4	8.90	262.78	297.93	63.98	127.6	150.00	303.27	332.74
5	12.80	258.08	284.59	64.13	127.53	149.30	301.26	323.76

$T'_{d,0}$ and $T_{d,0}$ are the temperatures of the onset of weight loss of PLLA-grafted SiO$_2$ and PLLA/PLLA-grafted SiO$_2$ nanocomposites, respectively. $T'_{d,max}$ and $T_{d,max}$ are the temperatures of the maximum rate of weight loss of PLLA-grafted SiO$_2$ and PLLA/PLLA-grafted SiO$_2$ nanocomposites, respectively. T_g, T_c, and T_m are glass transition temperature, crystallization temperature, and melting temperature of PLLA/PLLA-grafted SiO$_2$ nanocomposites, respectively. Temperatures are given in °C

[a] Mn of PLLA is 28457

Thermo-oxidative degradation of PLLA/PLLA-grafted SiO$_2$ nanocomposites

The thermo-oxidative stability of PLLA-grafted SiO$_2$, "free" PLLA, and PLLA/PLLA-grafted SiO$_2$ nanocomposites was investigated using a conventional non-isothermal gravimetric technique.

The grafting ratio of PLLA on silica particles had a significant effect on the thermo-stability of PLLA-grafted SiO$_2$, as seen from Table 2. $T'_{d,0}$ and $T'_{d,max}$ of PLLA-grafted SiO$_2$ increased with the increasing grafting ratio and exhibited the maximum value for run **4**. $T'_{d,0}$ and $T'_{d,max}$ of run **5** decreased probably because of its much lower grafting ratio and lower Mn of grafted PLLA. The temperatures of the onset and the maximum rate of weight loss of PLLA-grafted SiO$_2$ were much lower than that of pure PLLA except for run **4** close to that of pure PLLA, suggesting that SiO$_2$ particles had influenced the thermo-oxidative degradation of PLLA.

The existence of PLLA-grafted SiO_2 particles dramatically improved the thermo-oxidative degradation of PLLA/PLLA-grafted SiO_2 nanocomposites despite of the lower $T'_{d,0}$ and $T'_{d,max}$ of PLLA-grafted SiO_2, suggesting that the incorporation of PLLA-grafted SiO_2 with PLLA promoted the thermal stability of nanocomposites. $T_{d,0}$ and $T_{d,max}$ of PLLA/PLLA-grafted SiO_2 nanocomposites was much higher than that of pure PLLA and increased with the increasing SiO_2 Content except for run **5**. While, T_g, T_c, and T_m of nanocomposites varied slightly, compared with that of pure PLLA.

Conclusion

PLLA/PLLA-grafted SiO_2 nanocomposites were prepared by in situ melt polycondensation, in which SiO_2 powder was directly dispersed in 85% LLA by sonication. The aggregation of SiO_2 nanoparticles in the polycondensation process got serious with increasing SiO_2 content, which could be responsible for the decreasing Mn of grafted PLLA and "free" PLLA. SiO_2 content was critical parameter in this polycondensation system to achieve uniformly dispersed PLLA/PLLA-grafted SiO_2 nanocomposites.

The existence of PLLA-grafted SiO_2 had dramatically improved the thermo-oxidative stability of PLLA, while T_g, T_c, and T_m of PLLA/PLLA-grafted SiO_2 nanocomposites varied slightly.

References

1. Tsuji H, Bonfield W, Ikada Y, Smith R (2000) Porous biodegradable polyesters. 1. Preparation of porous poly(L-lactide) films by extraction of poly(ethylene oxide) from their blends. J Appl Polym Sci 75:629
2. Lunt J (1998) Large-scale production properties and commercial application of polylactic acid polymer. Polym Degrad Stab 59:145
3. Hiltunen K, Seppala JV, Harkonen M (1997) Effect of catalyst and polymerization conditions on the preparation of low molecular weight lactic acid polymers. Macromolecules 30:373
4. Vink ETH, Rabago KR, Glassner DA, Gruber PR (2003) Applications of life assessment to NatureWorks™ polylactide(PLA) production. Polym Degrad Stab 80:403
5. Neradovic D, Steenbergen MJV, Vansteetant L, Meijer YJ (2003) Degradation mechanism and kinetics of thermosensitive polyacrylamides containing lactic acid side chain. Macromolecules 36:7491
6. Zhao Y, Wang Z, Yang F (2005) Syntheses of poly(lactic acid)-poly(ethylene glycol) serial biodegradable polymer materials via direct melt polycondensation and their characterization. J Appl Polym Sci 97:195
7. Kim HS, Hwang MO, Kim MN, Yoon JS (2006) Preparation of high-molecular-weight poly(L-lactic acid)-based polymers through direct condensation polymerization in bulk state. J Appl Polym Sci 100:466
8. Zhou HJ, Rong MZ, Zhang MQ, Ruan WH, Friedrich K (2007) Role of reactive compatibilization in preparation of nanosilica/polypropylene composites. Polym Eng Sci 47:499

9. Zhao Y, Qiu Z, Yang W (2009) Effect of multi-walled carbon nanotubes on the crystallization and hydrolytic degradation of biodegradable poly(L-lactide). Compos Sci Technol 69:627

10. Wu CS, Liao HT (2007) Stydy on the preparation and characterization of biodegradable polylactide/multi-walled carbon nanotubes nanocomposites. Polymer 48:4449

11. Nakayama N, Hayashi T (2007) Preparation and characterization of poly(L-lactic acid)/TiO$_2$ nanoparticle nanocomposite films with high transparency and efficient photodegradability. Polym Degrad Stab 92:1255

12. Wu LB, Cao D (2008) 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. Polymer 49:742

13. Cao D, Wu L (2009) Poly(L-lactic acid)/silicon dioxide nanocomposite prepared via the in situ melt polycondensation of L-lactic acid in the presence of acidic silica sol: Isothermal crystallization and melting behaviors. J Appl Polym Sci 111:1045

14. Chen JH, Rong MZ, Ruan WH, Zhang MQ (2009) Interfacial enhancement of nano-SiO$_2$/polypropylene composites. Compos Sci Technol 69:252

15. Zhang G, Schlarb AK, Tria S, Elkedim O (2008) Tensile and tribological behaviors of PEEK/nano-SiO$_2$ composites compounded using a ball milling technique. Compos Sci Technol 68:3073

16. Mueller R, Kammler HK, Wegner K, Pratsinis S (2003) OH surface density of SiO$_2$ and TiO$_2$ by thermogravimetric analysis. Langmuir 19:160

17. Prucker O, Ruhe J (1998) Syntheses of poly(styrene) monolayers attached to high surface area silica gels through self-assembled monolayers of azo initiators. Macromolecules 31:592

18. Li CZ, Benicewicz BC (2005) Synthesis of well-defined polymer brushes grafted onto silica nanoparticles via surface reversible addition-fragmentation chain transfer polymerization. Macromolecules 38:5929