

Control of thermal degradation of poly(lactic acid) using functional polysilsesquioxane microspheres as chain extenders

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ABSTRACT: Two functional polysilsesquioxane microspheres, poly(epoxypropoxy)silsesquioxane (PESQ) and poly(epoxypropoxy/ami-no)silsesquioxane (PEASQ), were grafted onto commercial polylactic acid (PLA) via functional group reactions through melt processing and directly used as novel chain extenders to improve the thermal stability of PLA. During the whole reaction time of 35 min, the torques of P-2PESQ and P-1PEASQ were 60% higher than that of processed PLA. Thermal gravimetric analysis (TGA) revealed that the addition of PESQ or PEASQ into PLA increased the onset temperature for thermal degradation. PEASQ was found to be a potential chain extender for PLA. Compared with the processed PLA, the thermal decomposition temperatures of PEASQ modified PLA increased from 318 to 334°C at 5% weight loss. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41977.

KEYWORDS: addition polymerization; biopolymers and renewable polymers; degradation; rheology; thermal properties

Received 16 September 2014; accepted 15 January 2015

DOI: 10.1002/app.41977

INTRODUCTION

Over the past several decades, concerns on the exhaustion of petroleum resources and the environmental pollution from conventional plastic materials stimulate current intensive studies on biopolymers, which are biodegradable, biocompatible and based on renewable resources.^{1–4} Poly(lactic acid) (PLA) that can be synthesized from 100% renewable resources such as fermentation products of corn and sugar beets has attracted significant attention in environmental, biomedical, and pharmaceutical applications as well as alternatives to petro-based polymers.^{5–9} Compared with other biopolymers, PLA is easy to be processed, that is, PLA can be made into useful items using thermal processes such as extrusion and injection molding.^{10,11} However, one of the drawbacks of processing PLA in the molten state is its tendency to undergo thermal degradation, which are related to not only the processing temperature but also the residence time in the extruder and hot runner.¹¹ In other words, thermal, oxidative, and hydrolytic degradations may occur during processing which hinders the applications of PLA in practice by causing the cleavage of polymer chains and reduction in molecular weight.^{12,13} All these degradation processes could eventually result in deteriorations of rheological properties and mechanical properties of PLA.¹⁴

Generally, the rheological properties, especially the shear viscosity, have important effects on thermal processes. However, vari-

ous studies have shown that PLA degrades quickly at temperature above its melting point, which thus influences its shear viscosity vigorously.^{15,16} Despite all its advantages, the poor thermal stability of PLA poses considerable scientific challenges and limits their large-scale applications. Numerous efforts were taken to overcome such shortcomings, including nonreactive and reactive blending, copolymer synthesis and the addition of additives.^{17–20} One of the most convenient ways is to increase the molecular weight (M_w) during processing to compensate for the molecular weight decrease caused by processing degradation. For example, the free radical branching/linking of PLA has been introduced during the melt mixing process in an extruder or kneader in the presence of trace amounts of various peroxides as radical initiators.²¹ Also, the solid-state postpolymerization technique has been utilized to obtain high-molecular-weight PLA.²² Recently, “chain extenders,” the functional additives that are used to link the end groups of these low-molecular-weight PLA to obtain high-molecular-weight PLA, are considered to be an easy-to-apply alternative for many industries and have attracted much attention.^{23–25} Generally, the chain extenders have two or more functional groups, such as isocyanate,^{26,27} anhydride,^{28,29} amine,³⁰ and epoxy,¹⁸ to couple the two end groups of low-molecular-weight polymer chains³¹. Chain extenders not only offer an opportunity to enhance the physical and chemical properties of PLA by increasing the molecular weight but also introduce new functional groups into the PLA

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backbone paving the way for preparation of composites, laminates, coated items, and blends/alloys with improved properties and cost effectiveness.³²

Functional polysilsesquioxane (FPSQ), a micro- or nanosized functional organo-silicon, has been widely used to construct organic/inorganic hybrid materials.^{33–35} It has been widely used to improve the properties of polymers, for example, the glass transition temperature, thermal decomposition temperature, impact strength, and fire resistance.^{36,37} One of the outstanding properties shown by these hybrid materials is related to their thermal stability. The decomposition temperature of the organic polymeric phase increases due to the addition of the siloxane, which is investigated in PP, PMMA, and PS.^{38,39} Furthermore, FPSQ has no detrimental influence on the environmentally friendly property of PLA.⁴⁰ FPSQ has active functional groups, which can react with the end groups of PLA and thus lead to the chain extension of PLA. In other words, FPSQ affects the thermal property of PLA by forming both hybrid materials and chain extension. Whereas, to our best knowledge, it is the first time to employ FPSQ to modify commercial PLA in the hope of controlling its thermal degradation.

In this study, two kinds of FPSQ (i.e., with epoxy groups (PESQ) and with both epoxy and amino groups (PEASQ)) were synthesized by conventional one-step process and then grafted onto the commercial PLA through melt processing. The FPSQ-grafted PLA was employed as novel chain extension agents for the first time to improve the thermal stability of PLA. Optimization of different parameters to control thermal degradation of PLA, including the reaction time, temperature, additive concentration of PLA-FPSQ, and the different ratios of two functional groups, in PEASQ was systematically performed. The melt rheological properties were enhanced significantly with the addition of FPSQ. The results will be of referential importance to the design and synthesis of other functionalized material as chain extenders for the degradation of PLA.

EXPERIMENTAL

Materials

The PLA investigated, 2002D, was supplied by NatureWorks LLC, USA. The content of L-lactide is about 96 wt %, and the monomer is less than 0.3 wt %. Its glass transition temperature, (T_g), and melting temperature, (T_m), is 52°C and 148°C, respectively. The specific gravity and MFR are 1.12 and 9.2 (g·10 min⁻¹, 190°C, 2.16 kg). Epoxypropoxypropyltrimethoxysilane (EPTMS) and aminopropyltrimethoxysilane (APTMS) were purchased from Nanjing Capatue Chemical Co., Ltd, China and Diamond Advanced Material Of Chemical Inc., China, respectively. The FPSQs were synthesized from the two kinds of silane coupling agent EPTMS and APTMS. Ammonium hydroxide of analytical pure reagent grade was purchased from Shanghai Lingfeng Chemical Corp., China. All other chemicals were used as received.

Synthesis of Polysilsesquioxane Microspheres

poly(epoxypropoxy)silsesquioxane (PESQ) and poly(epoxypropoxy/amino)silsesquioxane (PEASQ) particles were prepared

using base catalyzed sol-gel process in aqueous medium.^{34,35} To synthesize the PESQ particles, 10 mL of EPTMS was added dropwise to 100 mL of water with a gentle stirring. One milliliter of ammonium hydroxide solution (NH₄OH, 25 wt %) was added to the above solution. As to PEASQ particles, 10 mL mixture of EPTMS and APTMS with different molar ratios was added to 100 mL of water. Then, to adjust the sample pH, ammonium hydroxide was added to the solution prepared earlier. After stirred for 24 h at room temperature, the resulting precipitate was filtrated with millipore filter membrane (0.22 μm) and rinsed thoroughly with distilled water and ethanol several times to remove the residual NH₄OH as well as unreacted monomers and oligomers. After freeze-dried at -50°C for 48 h, the PESQ particles and the PEASQ particles were obtained. According to the different molar ratios of APTMS in PEASQ from 10–40%, particles were named PEASQ1, PEASQ2, PEASQ3, and PEASQ4, respectively. The melting point of all particles was higher than 300°C.

Modified PLA Preparation

The commercial PLA was vacuum-dried in an oven (60°C) for 12 h before processed. Then, it was blended in the molten state with 0.5–4 wt % chain extenders in the rheocord (Thermo HaakeRheocord 300P+Rheomin600P, Germany), and the rotational speed was 60 rpm. The blendings were carried out under air atmosphere, with the temperature set to 180–210°C for 5–40 min. The products were placed in a vacuum oven (60°C) for at least 24 h. Disks with 25 mm diameter and 1.5 mm thickness were produced by compression molding at 190°C using a pressure of 10 MPa for 8 min. The molded samples were vacuum-dried again in an oven at 60°C before rheological characterization.

Characterization

FTIR Spectra Characterization. Fourier transform infrared spectroscopy (FTIR) measurements were taken on a spectrophotometer (iS10 FT-IR, Nicolet) at room temperature (ca. 25°C) using the KBr pellet method. FTIR absorption spectra were collected in the IR range from 4000 to 500 cm⁻¹. In all cases, 32 scans at a resolution of 1 cm⁻¹ were recorded.

Thermal Gravimetric Characterization. Thermal gravimetric analysis (TGA) was performed on a (SDT Q600, TA Instruments) thermal analyzer. Samples of 10–15 mg were heated from 20 to 800°C with a heating ramp of 10°C·min⁻¹ in air atmosphere.

Molecular Weight Characterization. The average molecular weight (M_w) and polydispersity index (PDI) of PLA samples were measured by gel permeation chromatography (PL-GPC50, Polymer Laboratories). The samples were dissolved in chloroform. Polystyrene standards were used to generate the calibration curve. These tests were conducted using chloroform as a carrier solvent at 35°C with a flow rate of 1 mL·min⁻¹.

Melt Flow Rate Characterization. The melt flow rate (MFR) of PLA samples was measured with MFR instrument (MI-4, Gottfert, Germany). Ten grams of sample was added into feed inlet, melt at 190°C for 5 min with 21.6 kg preloading force,

Table I. Abbreviations of Raw Material and Different Samples

Abbreviations	Full name
EPTMS	Epoxypropoxypropyltrimethoxysilane
APTMS	Aminopropyltrimethoxysilane
FPSQ	Functional polysilsesquioxane
PESQ	Poly(epoxypropoxy)silsesquioxane
PEASQ	Poly(epoxypropoxy/amino)silsesquioxane
PLA-PESQ	PESQ-modified PLA
PLA-PEASQ	PEASQ-modified PLA

then forced out from grinding mouth ($\varphi = 2.095$ mm) with 2.16 kg loading force.

Dynamic Rheological Characterization. Dynamic rheological measurements of the PLA samples were carried out using a strain-controlled rheometer (ARES, TA Instruments) with a $D = 25$ mm parallel plate geometry. About 5% strain was employed to ensure all tests were measured in linear region of PLA. To evaluate the thermal stability of the various systems, the storage modulus and complex viscosity were monitored as a function of time. The time sweep measurements were conducted under air atmosphere, at 180°C , using a frequency of 6.28 rads^{-1} and a gap of 1.5 mm. Frequency sweep tests over a frequency range of 0.1 – 100 rads^{-1} were also performed from high to low frequencies under the same conditions as stated previously. Dynamic rheological measurements of PLA samples were performed using a strain-controlled rheometer, from high to low frequencies, over a frequency range of 0.05 – 100 $\text{rad}\cdot\text{s}^{-1}$.

Mechanical Properties Measurement. The mechanical properties were measured according to ASTM test methods, such as D-638 for the tensile strength and D-790 for the flexural modulus, using a universal testing machine (MTS Systems, China). The Izod impact strength was tested on the basis of D-256 using an impact tester (MTS Systems, China). The reported values of the mechanical properties were averaged at five independent measurements.

Dispersibility Characterization. The dispersion of FPSQ in the PLA matrix of all samples was observed by FE-SEM (Nova Nano450, FEI Co.). The samples were freeze-fractured in liquid nitrogen and sputter coated with platinum.

^{29}Si NMR Characterization. ^{29}Si NMR spectra were measured at room temperature on a BrukerAvance 500 MHz spectrometer equipped with a Bruker solid-state accessory.

RESULTS AND DISCUSSION

Structure and Thermal Properties of PESQ and PEASQ Particles

The synthesis routes of PESQ and PEASQ particles (the meaning of abbreviations are listed in Table I) are illustrated in Supporting Information Scheme S1. Generally, hydrolytic precipitation of the trimethoxysilanes in water or ethanol/water is quite fast under base conditions.^{35,41,42} Initial hydrolysis of the EPTMS and APTMS results in silanol oligomers. Silanol

(Si—OH) is highly reactive and tends to form polysilsesquioxanes in the presence of base catalyst. The amino groups of APTMS may increase the pH of solution and accelerate the hydrolytic coprecipitation process. Simultaneous hydrolysis of APTMS and EPTMS led to coprecipitation, but the product was different with variation of APTMS/EPTMS molar ratios. When the APTMS molar ratio in the precursors is less than 30%, white precipitate appears. However, the coprecipitation products do not precipitate from solution when the molar ratio of APTMS in the precursors is 40% due to the excellent solubility of coprecipitation PEASQ in water.⁴³

According to the IR spectra of PESQ particles (Supporting Information Figure S1), it was found that PESQ exhibited well-defined methyl group at 2939 cm^{-1} ($\nu\text{C—H}$), 1413 cm^{-1} ($\delta\text{C—H}$ in Si—R), ca. 1119 – 1127 cm^{-1} , ca. 1032 – 1036 cm^{-1} ($\nu\text{Si—O—Si}$), and 791 cm^{-1} ($\nu\text{Si—C}$). Si—O—Si stretching peaks at 1119 – 1127 cm^{-1} indicated the presence of cage structure, while adsorption ones at 1032 – 1036 cm^{-1} showed that the ordered structure was like probable ladder or layered.^{44,45} The asymmetric ring stretching vibration of epoxy group was at 909 cm^{-1} .⁴⁶

The same adsorption of Si—O—Si structure and epoxy group existed in PEASQ. The spectrum of PEASQ showed clue due to aminopropyl group at 1482 cm^{-1} ($\delta\text{N—H}$), 3376 cm^{-1} ($\nu\text{N—H}$), 2934 and 2970 cm^{-1} ($\nu\text{C—H}$). A broad band around 3400 cm^{-1} could be attributed both to the adsorbed water and to the Si—OH group,⁴⁷ nearby the —NH— group ($\nu\text{N[sond]H}$, 3376 cm^{-1}). The enhanced adsorption of 3400 cm^{-1} resulted from increase in APTMS molar ratio indicates the increase in aminopropyl group.

Furthermore, in order to avoid the intensity influence of different particles in IR spectra, 1034 cm^{-1} of Si—O—Si was chosen as a standard peak. Relative intensity (RI) of aminopropyl group was calculated using the following eq. (1) H represented the peak height.

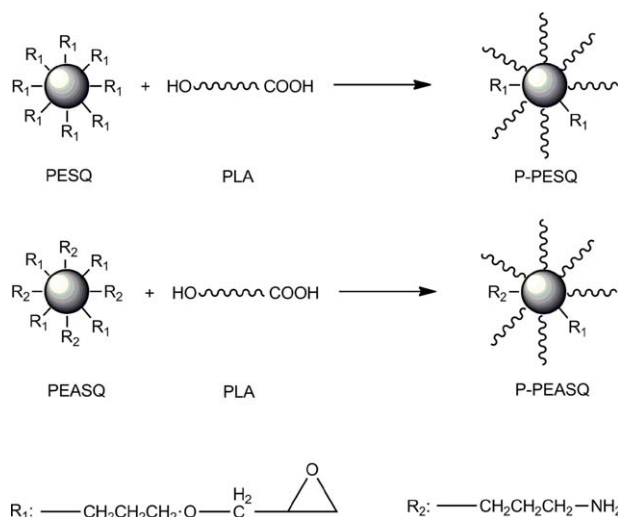
$$RI = H_{3400}/H_{1034} \quad (1)$$

According to Table II, the RI data raised with the increase in the amount of APTMS in general.

Solid-state ^{29}Si NMR analysis is a powerful method to characterize the chemical structure of polysilsesquioxane frameworks. Caravajal *et al.*⁴⁸ reported the ^{29}Si NMR spectra exhibited major peaks in the regions of -66 , -58 , and -49 ppm, due to the silicons of the attached $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}$ moiety of APTES-modified silica. According to Lu *et al.*'s work,⁴³ the ^{29}Si NMR spectrum of poly(aminopropyl/methyl)silsesquioxane particles showed that there were a large peak at -62.1 ppm and a weak shoulder peak at about -53 ppm, which were assigned to fully condensed T3 and linear T2 species, respectively.

Table II. Relative Aminopropyl Ratio of PEASQ Particles

	PESQ	PEASQ1	PEASQ2	PEASQ3	PEASQ4
RI	0.23	0.35	0.40	0.60	0.91



Scheme 1. Processing illustration of PLA grafted by PESQ (PLA-PESQ) and PEASQ (PLA-PEASQ).

Supporting Information Figures S2(a,b) are the ^{29}Si NMR spectra of PESQ and PEASQ3 particle. One large peak at -71.9 ppm was found for PESQ (Supporting Information Figure S2a), suggesting that PESQ particle enjoys a T3 structure. However, PEASQ3 shows a large peak at -70.1 ppm and a weak shoulder peak at -61.7 ppm (Supporting Information Figure S2b), assigned to fully condensed T3 (70.5%) and linear T2 (29.5%) species, respectively. In conclusion, the formation of T1 and T0 species was insignificant, suggesting that the coprecipitation of PESQ and PEASQ was quite completed.⁴⁹

Supporting Information Table S1 represents the amino group content and particle size of polysilsesquioxanes particles. The amino group contents of PEASQ particles determined by Element Analysis (vario EL III, Elementar, Germany) were found to be slightly lower than the theoretical values. The results could be due to the excellent solubility of APTMS and its hydrolysis/condensation products in water.⁵⁰ These results were consistent with those reported by Liu *et al.*⁴⁵

Scanned electron microscope (SEM) images showed the morphology of polysilsesquioxanes particles (Figure 2). The PESQ particles prepared from EPTMS alone are spherical with a medium size about $2.2 \mu\text{m}$ (Supporting Information Figure S3a), but a bit particle aggregation existed. The particle aggregation was quite evident for the copolymerized PEASQ particles, and the particle size decreased with the increasing of the APTMS amount in the APTMS/EPTMS mixtures, as shown in Supporting Information Figure S3(b–d). The results could be due to the excellent solubility of APTMS in water, which made the PEASQ particles more hydrophilic. Additionally, the amino groups of APTES raised pH of reaction solution and catalyzed the hydrolytic cocondensation reactions of APTMS and EPTMS. Increasing in hydrolysis rates with increasing pH led to a higher nucleation rate, which also resulted in a larger number of particles but a smaller final particle size.³⁵ Moreover, it was found in Supporting Information Figure S3e, when the APTMS molar

ratio in the precursors reached 40%, most particles became gel, and formed larger particles after drying.

The thermal stability of PESQ and PEASQ particles in air atmosphere was determined by TGA (Supporting Information Figure S4). The weight loss in the 100 – 250°C range for polysilsesquioxane was probably ascribed to the residual reaction of alkoxysilyl groups.^{44,49} The thermal reduction of polysilsesquioxane in the range of 250 – 700°C appeared, mainly due to the decomposition of organic moieties groups.³⁵ The thermal decomposition temperatures of the PESQ particles in air atmosphere, at 1, 5, and 10% weight loss were 250 , 272 , and 282°C , respectively. The thermal decomposition temperatures of the PEASQ particles, at 1, 5, and 10% weight loss were 182 , 265 , and 284°C , respectively. The TGA result showed the good thermal stability of polysilsesquioxane microspheres as the 5% weight loss temperature is much higher than the processing temperature of PLA (around 200°C).

The Effect of Reaction Conditions on PLA-PESQ

The functional polysilsesquioxane microspheres, PESQ and PEASQ, were grafted onto commercial PLA via functional group reactions through melt processing. The processing route of PLA grafted by PESQ (PLA-PESQ) and PEASQ (PLA-PEASQ) is illustrated in Scheme 1. The functional polysilsesquioxane microspheres were directly used as novel chain extenders to improve the thermal stability of PLA.

The effects of reaction conditions, including reaction time, additive concentration, and reaction temperature, on the rheological properties of PLA grafted by PESQ (PLA-PESQ) were investigated.

Reaction Time. The dynamic shear viscosity analysis is a general method to investigate the thermal degradation of PLA.⁵¹

Compared with neat PLA, the dynamic shear viscosity of PLA-PESQ (Figure 1) was improved dramatically. The low-frequency range of frequency sweep curve indicates the existence of branched structure.⁵² The plot also shown increasing M_w caused by chain extension reaction compensated for the M_w decrease

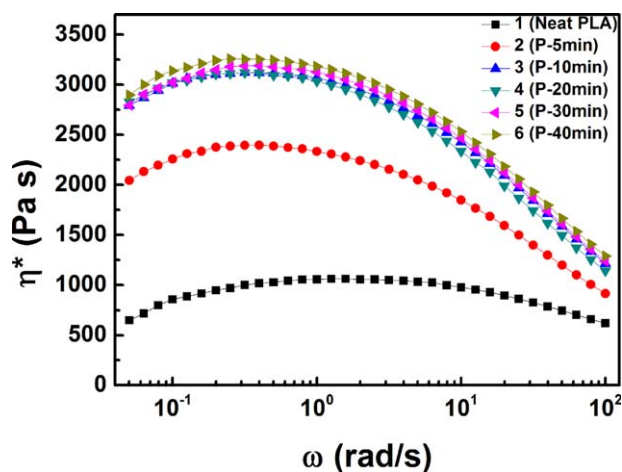


Figure 1. Dynamic frequency sweeps of neat PLA and PESQ-modified samples for different reaction time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

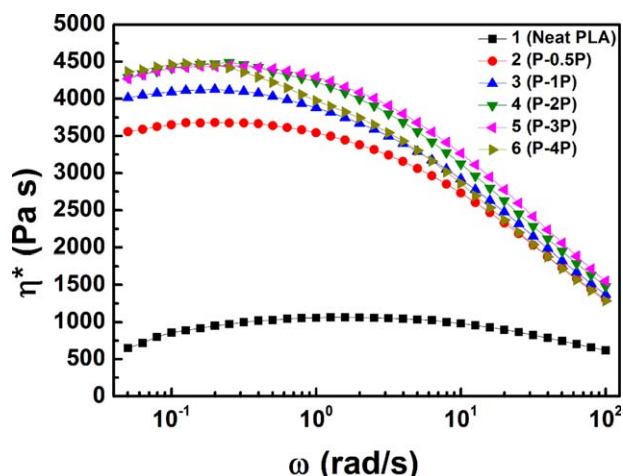


Figure 2. Dynamic frequency sweeps of neat PLA and PESQ-modified samples for different additive concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

caused by processing degradation during 10–40 min, which also led to the increase in melt viscosity. With the increase in reaction time, there was only a slight change in M_w (Table III), between $200.0 \text{ kg}\cdot\text{mol}^{-1}$ and $220.0 \text{ kg}\cdot\text{mol}^{-1}$, which indicates the inhibited degradation of PLA by adding PESQ as chain extenders. It is widely accepted that the M_w decreased with thermal degradation. During the processing, PESQ could work as a chain extender to covalently bond the segments of PLA through functional group reaction. As a joint result of thermal degradation and chain extension, the M_w of PLA reached a balance. MFR is decided by both M_w and molecular structure. Branched or crosslinking structure or large M_w leads to a low MFR. With the increase in reaction time, MFR of PLA-2PESQ (Table III) showed a very slight increasing. It means that the cleavage of molecular chain and the formation of branched structure reached a balance. The MFR showed a minimum of $3.8 \text{ g}\cdot 10\text{min}^{-1}$ at 5 min.

Additive Concentration. Secondly, the influence of the additive concentration of PESQ on the grafting reaction has been investigated. Compared with neat PLA, shear viscosity (Figure 2) of each PLA-PESQ sample increased which implied the formation of branched structure. A positive correlation between viscosity

Table III. The Effects of Reaction Time on the Properties of PESQ-Modified PLA

Samples	Reaction time (min)	M_w ($\text{kg}\cdot\text{mol}^{-1}$)	PDI	MFR ($\text{g}\cdot 10\text{min}^{-1}$)
1	0	97.4 ± 2.7	3.3 ± 0.2	8.1 ± 0.3
2	5	213.0 ± 4.2	1.7 ± 0.1	3.8 ± 0.1
3	10	209.2 ± 3.1	1.7 ± 0.1	4.0 ± 0.1
4	20	219.3 ± 3.5	1.6 ± 0.1	4.0 ± 0.1
5	30	206.6 ± 3.9	1.7 ± 0.2	4.3 ± 0.2
6	40	216.3 ± 2.7	1.7 ± 0.2	4.4 ± 0.2

Reaction temperature is 190°C .
Additive concentration is 2 wt %.

Table IV. The Effects of Additive Concentration on the Properties of PESQ-Modified PLA

Samples	Additive concentration (wt %)	M_w ($\text{kg}\cdot\text{mol}^{-1}$)	PDI	MFR ($\text{g}\cdot 10\text{min}^{-1}$)
1	0	97.4 ± 2.7	3.3 ± 0.2	8.1 ± 0.3
2	0.5	137.8 ± 2.7	2.3 ± 0.1	4.2 ± 0.1
3	1	182.2 ± 4.0	1.9 ± 0.1	4.0 ± 0.2
4	2	209.2 ± 3.1	1.7 ± 0.1	4.0 ± 0.1
5	3	152.3 ± 3.9	2.1 ± 0.2	3.7 ± 0.1
6	4	154.0 ± 2.7	2.1 ± 0.1	3.6 ± 0.2

Reaction temperature was 190°C .
Reaction time was 10 min.

and additive concentration was found below the content of 2 wt %, while a plain appeared after 2 wt %. With the increase in PESQ content, the M_w (Table IV) showed a maximum of $209.2 \text{ kg}\cdot\text{mol}^{-1}$ at 2 wt %, which demonstrate that 2 wt % PESQ was enough to obtain desired product. Furthermore, MFR (Table IV) showed a minimum of $3.6 \text{ g}\cdot 10\text{min}^{-1}$ at 4 wt %.

Reaction Temperature. Finally, the effects of processing temperature on PLA-PESQ have also been studied. The rheological properties (Figure 3) showed the same trend as M_w , and the dynamic shear viscosity showed the maximum value at 200°C , which indicated the optimized temperature for more adequate reaction and higher degree of branching. With the increase in the reaction temperature, the M_w increased first then decreased (Table V). The maximum M_w of PLA obtained is $250.4 \text{ kg}\cdot\text{mol}^{-1}$ at 200°C , which can be attributed to the competition between the reaction rate and the thermal degradation of PLA. The MFR (Table V) showed the minimum of $3.9 \text{ g}\cdot 10\text{min}^{-1}$ at 200°C .

According to the results of shear viscosity, M_w and MFR, the reaction time, reaction temperature, and additive concentration of PLA-PESQ were optimized to 10 min, 200°C and 2 wt %.

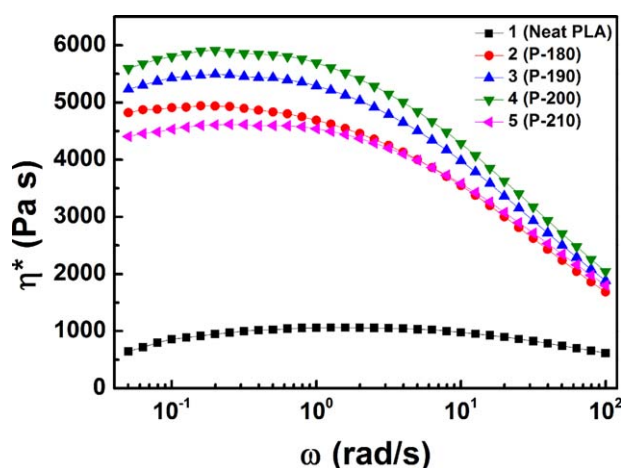


Figure 3. Dynamic frequency sweeps of neat PLA and PESQ-modified samples for different reaction temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. The Effects of Reaction Temperature on the Properties of PESQ-Modified PLA

Samples	Reaction temperature (°C)	M_w (kg·mol ⁻¹)	PDI	MFR (g·10min ⁻¹)
1	/	97.4 ± 2.7	3.3 ± 0.2	8.1 ± 0.3
2	180	81.3 ± 2.1	6.5 ± 0.1	4.4 ± 0.2
3	190	209.2 ± 3.1	1.7 ± 0.1	4.0 ± 0.1
4	200	250.4 ± 4.4	1.5 ± 0.2	3.9 ± 0.1
5	210	208.3 ± 2.5	1.8 ± 0.2	5.2 ± 0.2

Sample 1 is neat PLA.
Additive concentration is 2 wt %.
Reaction time is 10 min.

The corresponding shear viscosity of modified PLA was 4500 Pas, which was approximately six times that of neat PLA. The M_w of PLA-PESQ was 250.4 kg·mol⁻¹, twice of neat PLA. The MFR was 3.9 g·10min⁻¹, reduced to about half of neat PLA.

The Effects of Reaction Conditions on PLA-PEASQ

The effects of various PEASQ particles on the properties of PLA grafted by PEASQ (PLA-PEASQ) were investigated. From the rheological properties of PLA-PEASQ (Figure 4), it was found that dynamic shear viscosity was greatly improved after processed for 10 min at 190°C compared with neat PLA. From the plot of viscosity (η) versus frequency (ω) in low frequency, P-1PEASQ3 showed the highest dynamic shear viscosity, which was the best rheological property to inhibit degradation in all our FPSQ particles. With the increase in amino group contents in PEASQ, there was a remarkable change in M_w (Table VI) of P-1PEASQ2 and P-1PEASQ3 were up to 191.5 and 211.7 kg·mol⁻¹, respectively. In comparison, the M_w of neat PLA was just 97.4 kg·mol⁻¹. At the same time, the MFR showed a minimum of 4.5 g·10min⁻¹ in P-1PEASQ2 and P-1PEASQ3.

The amino group molar ratio may also influence the rheological properties of PLA-PEASQ. Two hypotheses were proposed as

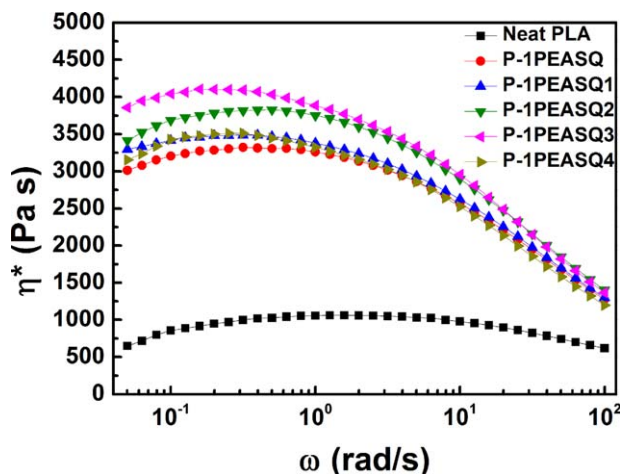


Figure 4. Dynamic frequency sweeps of neat PLA and different PEASQ-modified samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VI. The Effects of Different PEASQ on the Properties of PEASQ-Modified PLA

Samples	M_w (kg·mol ⁻¹)	PDI	MFR (g·10min ⁻¹)
Neat PLA	97.4 ± 2.7	3.3 ± 0.2	8.1 ± 0.3
Processed PLA	104.8 ± 3.5	2.2 ± 0.1	7.5 ± 0.2
P-1PEASQ	182.2 ± 2.9	1.9 ± 0.1	4.0 ± 0.1
P-1PEASQ1	101.4 ± 2.2	3.9 ± 0.2	3.9 ± 0.1
P-1PEASQ2	191.5 ± 3.7	2.2 ± 0.1	3.6 ± 0.1
P-1PEASQ3	211.7 ± 3.8	1.8 ± 0.2	3.6 ± 0.1
P-1PEASQ4	126.8 ± 2.8	2.9 ± 0.1	4.0 ± 0.1

Additive concentration was 1wt %.
Reaction time was 10 min.
Reaction temperature was 190°C.

follows: (1) particle size might influence reactivity; (2) the amino group could accelerate degradation of PLA.

According to part 3.1, the particle size of PEASQ decreases with the increase in amino group contents of PEASQ, from PEASQ1 to PEASQ3. The particle size of PESQ was larger than PEASQ-1. The particle size of PEASQ-4 was much larger than other particles due to the severe particle aggregation. In conclusion, the smallest size belonged to PEASQ-3, which has the best rheological properties. Small particle size will bring large specific surface area, which may be benefit to fully reaction.

In order to figure out the influence of particle size, well-dispersed PESQ particles with different particle size (Supporting Information Figure S5) were synthesized by acid-base two-step sol-gel process in aqueous medium. With the increase in particle size, the poly(epoxypropoxy)silsesquioxane were named PESQ-1, PESQ-2, PESQ-3, and PESQ-4. The MFR of different PESQs-modified PLA was shown in Figure 5. There was a slight change on MFR, indicating that particle size was not the primary factor in the range of 0.5–2.5 μ m.

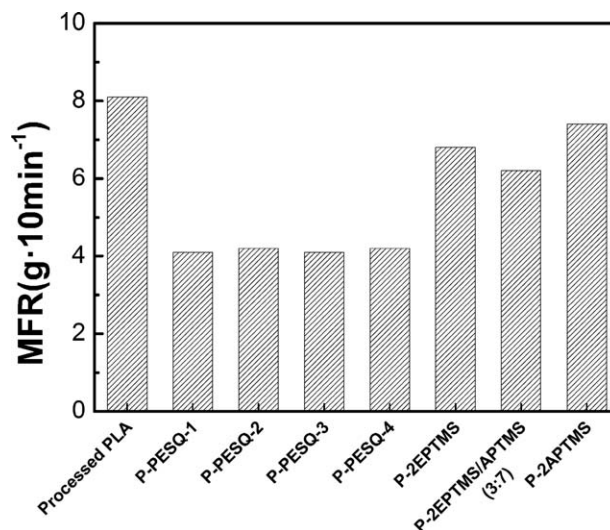


Figure 5. MFR of PLA and modified PLA processed for 10 min at 200°C.

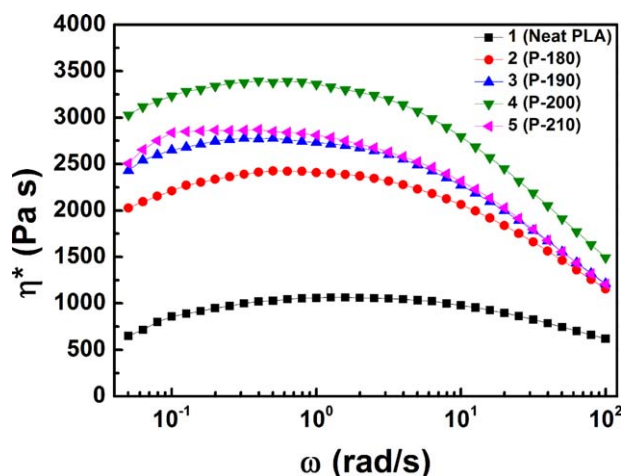


Figure 6. Dynamic frequency sweeps of neat PLA and modified PEASQ samples for different reaction temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In order to confirm the impact of amino group contents of PEASQ particles on PLA degradation, silane-coupling agent was used to process with PLA directly, the silane-coupling agent pre-reacted under vacuum at 80°C for 1 h. The MFR was shown in Figure 10. It was found that two kinds of silane-coupling agent (P-2EPTMS/APTMS(7 : 3)) provide higher reactivity than only APTMS(P-2APTMS) or EPTMS(P-2EPTMS). P-2APTMS had lower MFR than P-2EPTMS cause of aminopropyl group. Putting it briefly, the amino group aggravates degradation of PLA, which was also reported by Hong.⁵³

In summary, hypothesis of amino group contents is valid. Thus, P-PEASQ3 is expected to offer better rheological properties among all PEASQ-modified PLA. We used PEASQ3 as the chain extender in following experiment.

Reaction Temperature. First, the optimal reaction condition of PLA-PEASQ was examined, including the reaction time, additive concentration, and reaction temperature. With the increase in temperature, the values of shear viscosity first increased and then decreased, which was similar to PESQ. The dynamic shear viscosity (Figure 6) showed the maximum value at 200°C, which indicated that optimized temperature for more adequate

Table VII. The Effects of Reaction Temperature on the Properties of PEASQ-Modified PLA

Samples	Reaction temperature (°C)	M_w (kg·mol ⁻¹)	PDI	MFR (g·10min ⁻¹)
1	/	97.4 ± 2.7	3.3 ± 0.2	8.1 ± 0.3
2	180	91.7 ± 1.9	5.4 ± 0.1	4.4 ± 0.2
3	190	211.7 ± 3.8	1.8 ± 0.2	3.6 ± 0.1
4	200	198.3 ± 3.9	1.7 ± 0.1	3.6 ± 0.1
5	210	168.5 ± 3.5	1.9 ± 0.2	4.0 ± 0.1

Sample 1 is neat PLA.
Additive concentration is 1 wt %.
Processing time is 10 min.

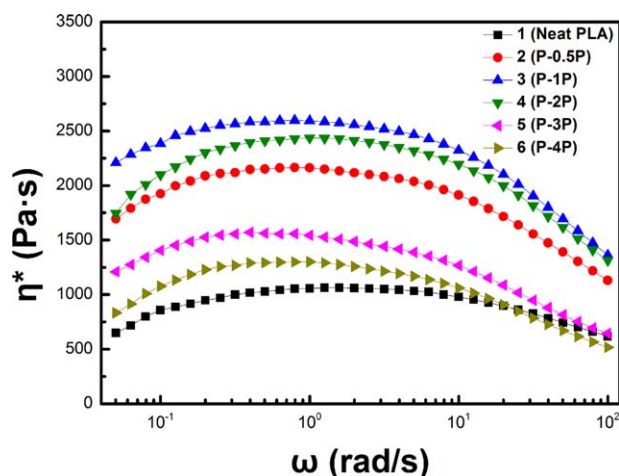


Figure 7. Dynamic frequency sweeps of neat PLA and PEASQ-modified samples for different additive concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reaction and higher degree of branching was 200°C. At low temperature, reaction cannot fully processed thus led to low shear viscosity, while at high temperature PLA degraded drastically, also presented low shear viscosity. With the increase in the reaction temperature, the M_w (Table VII) showed the maximum of 198.3 kg·mol⁻¹ at 200°C, which also can be attribute to the competition of the reaction rate and the thermal degradation of PLA. As expected, the MFR (Table VII) showed the minimum of 3.6 g·10min⁻¹ at 190°C and 200°C.

Additive Concentration. The additive concentrations of PEASQ were studied from 0.5 to 4 wt % (Figure 7). It is found that 1 wt % was the best addition amount for PLA-PEASQ. About 0.5 wt % PEASQ was not enough for this reaction, while the high additive concentration of PEASQ would aggravate PLA degradation, which was influenced by the side effect of increasing amino group content. A negative correlation between MFR and additive concentration was found when the content was beyond 1 wt %. The M_w and MFR (Table VIII) showed the best performance at 1 wt %, which were 198.3 kg·mol⁻¹ and 3.6 g·10min⁻¹, respectively. The results indicated that a large amount amino groups will aggravate the degradation of PLA.

Table VIII. The Effects of Additive Concentration on the Properties of PEASQ-Modified PLA

Samples	Additive concentration (wt %)	M_w (kg·mol ⁻¹)	PDI	MFR (g·10min ⁻¹)
1	0	97.4 ± 2.7	3.3 ± 0.2	8.1 ± 0.3
2	0.5	129.4 ± 3.7	2.6 ± 0.1	5.2 ± 0.2
3	1	198.3 ± 3.9	1.7 ± 0.1	3.6 ± 0.1
4	2	180.7 ± 2.9	1.6 ± 0.2	3.8 ± 0.1
5	3	153.0 ± 3.5	2.0 ± 0.1	4.9 ± 0.2
6	4	144.1 ± 3.6	2.2 ± 0.1	4.9 ± 0.2

Reaction temperature is 200°C.
Reaction time is 10 min.

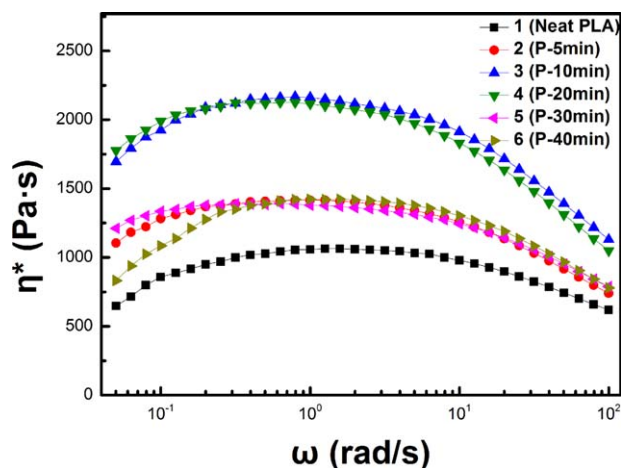


Figure 8. Dynamic frequency sweeps of neat PLA and PEASQ-modified samples at different reaction time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Reaction Time. The relationship between rheological properties of PLA-PEASQ and reaction time were also investigated (Figure 8). From the plot of viscosity (η) versus frequency (ω) in low frequency, the existence of branched structure could be speculated. The shear viscosity reached to a high level during 10–20 min, since increasing M_w in reaction compensate for the degradation of M_w . The reaction cannot fully process during 5 min, while PLA begin to degrade seriously after 30 min reaction time. With the increase of reaction time, the M_w (Table IX) showed the maximum of $198.3 \text{ kg}\cdot\text{mol}^{-1}$ at 10 min. MFR (Table IX) showed a minimum of $3.6 \text{ g}\cdot 10\text{min}^{-1}$ at 10 min.

According to the values of shear viscosity, M_w and MFR, the reaction time, temperature, and the additive concentration of PLA-PEASQ3 were optimized to 10 min, 200°C and 1 wt %.

Dispersibility of FPSQ in PLA

Figure 9 displays SEM images of fractured surfaces of the modified PLA after process during the optimal condition. PLA-PESQ

Table IX. The Effects of Reaction Time on the Properties of PEASQ-Modified PLA

Samples	Reaction time(min)	M_w ($\text{kg}\cdot\text{mol}^{-1}$)	PDI	MFR ($\text{g}\cdot 10\text{min}^{-1}$)
1	0	97.4 ± 2.7	3.3 ± 0.2	8.1 ± 0.3
2	5	161.3 ± 2.9	2.2 ± 0.2	4.6 ± 0.1
3	10	198.3 ± 3.9	1.7 ± 0.1	3.6 ± 0.1
4	20	186.9 ± 3.1	1.6 ± 0.1	5.1 ± 0.2
5	30	178.0 ± 4.6	1.8 ± 0.2	5.9 ± 0.2
6	40	173.8 ± 5.8	2.1 ± 0.3	7.0 ± 0.3

Reaction temperature was 200°C .
Additive concentration was 1wt %.

showed a relative rough fractured surface without any aggregations of PESQ particles. PLA-PEASQ exhibited a smooth fractured surface due to the smaller particle size of PEASQ. It confirms that two kinds of polysilsesquioxane are dispersed homogeneously in the PLA matrix.

Investigation of PLA Thermal Degradation

In order to simulate the degradation of modified PLA during processing, the rheocord was used to monitor the dynamic evolution of the torque during the reaction process (Figure 10a). As the reaction during the addition of reactants was negligible, the moment when rotation speed reaches 60 rpm was treated as the origin of reaction time.

Since the torque value was proportional to the apparent viscosity of materials, which depended on the M_w and chain structure of polymer, a dramatic increase in torque certainly indicated the production of the longer chains or even a small number of LCB in reaction system. During the whole reaction time of 35 min at 200°C , the torques of P-2PESQ and P-1PEASQ were 60% higher than that of Processed PLA (Figure 10a), owing to the extending or branching of PLA chains. All the torques decreased monotonously with the reaction time, which may ascribe to the possible thermal degradation of PLA

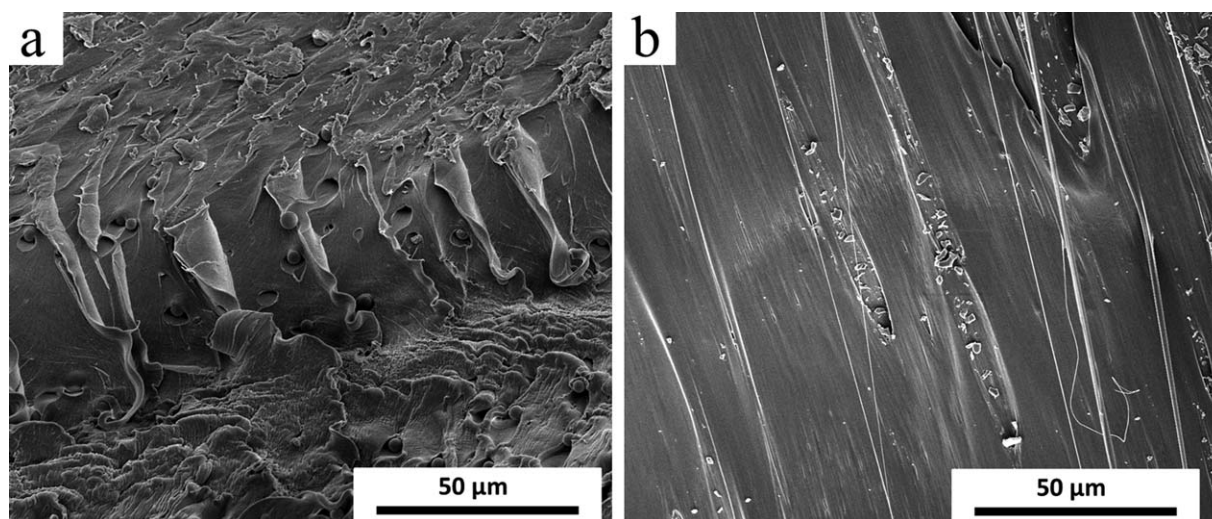


Figure 9. SEM images of the fracture surfaces of (a) PLA-PESQ, (b) PLA-PEASQ.

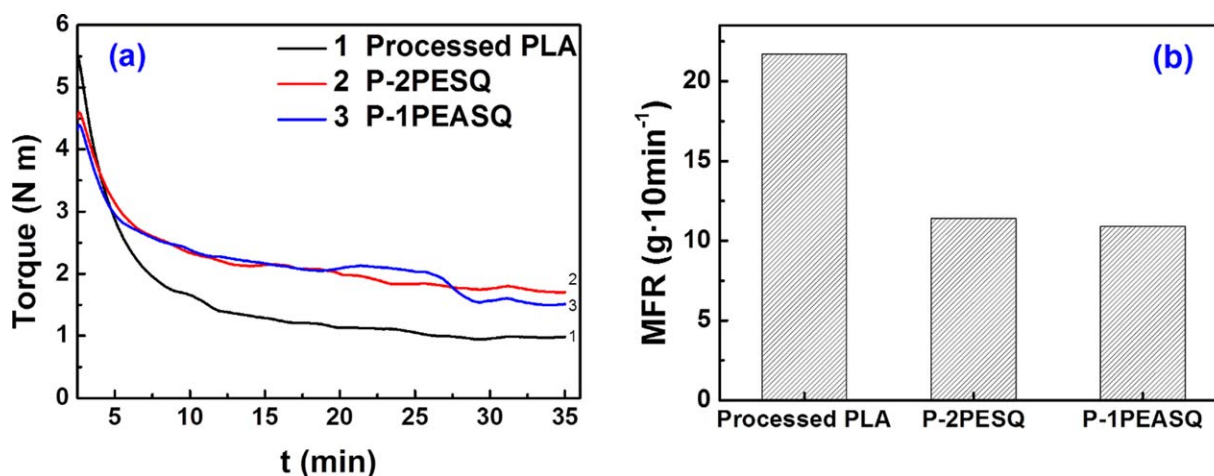


Figure 10. (a) Torque evolutions for processed PLA and modified PLA reaction courses. (b) MFR of PLA and modified PLA processed for 35 min at 200°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

during processing. During the first 27 min, the thermal stability of P-1PEASQ was better, while after 27 min, P-2PESQ performed better. This possibly because that amino group may not only act as chain extender but also aggravate degradation. At the first 27 min, the reaction between amino group and PLA was in dominant. While after 27 min, the other was in dominant.

The optimal reaction condition of PESQ and PEASQ with PLA was confirmed. To investigate which additive was more effective, the MFR after 35 min processed in rheocord was tested. As shown in Figure 10b, the MFR of PLA processed for 35 min (Processed PLA) was 21.7 g·10min⁻¹, about twice than neat PLA. It means that serious thermal degradation happened during processing. The MFR of modified PLA, however, increased only a small amount, which showed fine performance in control thermal degradation. By comparison, PEASQ is more effective than PESQ due to its less dosage and better performance.

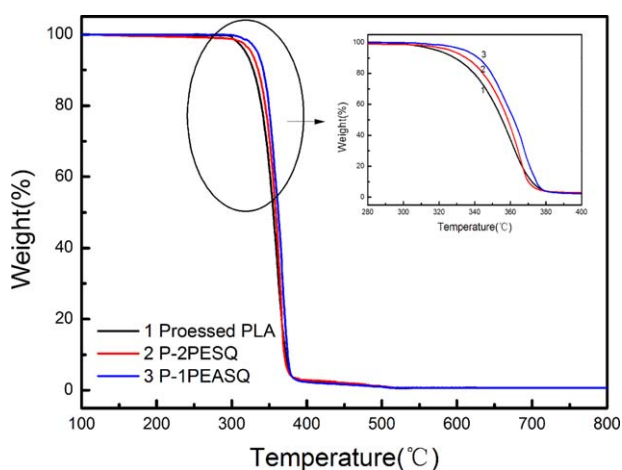


Figure 11. TGA curves of PLA and modified PLA processed for 10 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The thermal stability of the processed PLA and modified PLA in air atmosphere was investigated using TGA (Figure 11). Weight loss mainly takes place in the 300–400°C range. The thermal decomposition temperatures of processed PLA, at 1, 5, and 10% weight loss were 316, 318, and 329°C, respectively. While the thermal decomposition temperatures of P-2PESQ-200-10 min, at 1, 5, and 10% weight loss were 323, 326, and 335°C, respectively, the thermal decomposition temperatures of P-1PEASQ-200-10 min, at 1, 5, and 10% weight loss were 324, 334, and 342°C, respectively. The thermal decomposition temperature increased about 10°C compared with processed PLA. The TGA result showed that modified PLA has better thermal stability than unmodified PLA. Moreover, P-PEASQ has better thermal stability than P-PESQ. The results indicated that PEASQ is a more effective extender to control the thermal degradation of PLA.

Mechanical Properties of PLA

Furthermore, the impact strength (Table X) of P-2PESQ was increased to 52 J·m⁻¹, two times larger than that of neat PLA, indicating a dramatically enhanced toughness. As to P-2PESQ, much more FPSQ was added into PLA matrix than P-1PEASQ. Besides, compared with PEASQ, PESQ has longer chain on the surface, because of higher M_w . Both of these lead to more branched chain, thus causing higher cross linking with PLA chain. So P-2PESQ has higher mechanical properties and more toughness than P-1PEASQ.

Table X. The Mechanical Properties of Neat PLA and Optimal Modified PLA

Samples	Impact strength (J·m ⁻¹)	Flexural modulus (MPa)	Tensile strength (MPa)
Neat PLA	25 ± 1	2697 ± 14	44 ± 2
P-2PESQ	52 ± 1	2701 ± 16	40 ± 1
P-1PEASQ	46 ± 1	2677 ± 10	39 ± 1

CONCLUSIONS

PESQ and PEASQ were grafted onto commercial PLA via functional group reactions and employed as the chain extenders to improve the thermal degradation through melt processing. Based on the rheological, M_w and MFR results, the reaction time, temperature, and the additive concentration of PLA-PESQ were optimized to 10 min, 200°C and 2 wt %, respectively, while the processing conditions of PLA-PEASQ were optimized to 10 min, 200°C and 1 wt %. Results showed that the shear viscosity of PLA-PESQ in low-frequency range increased from 750 to 5500 Pas, approximately six times larger than that of neat PLA. In addition, the shear viscosity of PLA-PEASQ was 33% higher than that of PLA-PESQ. The M_w of both PLA-PESQ and PLA-PEASQ was nearly tripled compared to the M_w of neat PLA. Moreover, during the whole reaction time of 35 min, the torques of P-2PESQ and P-1PEASQ were 60% higher than that of Processed PLA. TGA revealed that the addition of PESQ or PEASQ into PLA increased the onset temperature of thermal degradation. PEASQ was found to be a more efficient chain extender, the thermal decomposition temperatures at 5% weight loss was 334°C, about 16°C higher. Finally, the impact strength was increased to twice of that of neat PLA, indicating that the toughness was significantly enhanced.

ACKNOWLEDGMENTS

This study is financially supported by the National Natural Science Funds of China (21106042, 21306047, 21476085, U1162110), Program of Shanghai Subject Chief Scientist (XD1401500), and Fundamental Research Funds for the Central Universities of China (WA1214051, WA1314051).

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