

Thermal Stability of Modified End-Capped Poly(lactic acid)

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ABSTRACT: The influence of functional end groups on the thermal stability of poly(lactic acid) (PLA) in nitrogen- and oxygen-enriched atmospheres has been investigated in this article using differential scanning calorimetry, thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). Functional end groups of PLA were modified by succinic anhydride and L-cysteine by the addition–elimination reaction. PLA was synthesized by azeotropic condensation of L-lactic acid in xylene and characterized by nuclear magnetic resonance. The values of the activation energies determined by TGA in nitrogen and oxygen atmospheres revealed that the character of functional end groups has remarkable influence on the thermal stability of PLA. Moreover, DMA confirmed the strong influence of functional end groups of PLA on polymer chains motion. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41105.

KEYWORDS: differential scanning calorimetry (DSC); thermal properties; thermogravimetric analysis (TGA)

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INTRODUCTION

In recent years, biodegradable polymers have been investigated extensively for their potential applications in medical, pharmaceutical, and packaging fields. Polylactic acid (PLA) is one of the most important bio-based biodegradable thermoplastic polymers with mechanical properties comparable to conventional petroleum-based plastics like polypropylene and polyethylene terephthalate. Chemical and physical properties of products based on PLA generally depend on the polymerization process, resulting tacticities, macromolecular characteristics, crystal structure, crystallinity concentration, the presence of additives, and processing technology. Despite the large variety of commercially available PLA grades, the applicability of PLA is still limited by its severe brittleness, low heat distortion temperature, slow crystallization rate, and relatively high production costs. Literature offers a number of research works devoted to modification of PLA by polymerization, copolymerization, blending, and composite processing technologies. The main discussed properties of polylactides and their related samples are structure, molecular weight properties, thermal properties, mechanical properties, and biodegradation behavior.^{1–9} The effect of different modifications of PLA in terms of thermal properties was studied mainly as a change in glass transition temperature, crystallization, and melting behavior. Nevertheless, the changes in the thermal stability of PLA in regard to the presented synthesis methods, new additives, or polymer processing methods were only rarely studied. The thermal degradation is a complex process depending on the involved conditions such as temperature, time, and kind of environment. As the main

mechanism of PLA, thermal degradation is considered the intramolecular transesterification with the formation of cyclic oligomers and by-products like acrylic acid, carbon oxide, and acetaldehyde. Intra- and intermolecular ester exchange, cis-elimination, radical and concerted non-radical reactions, and Sn-catalyzed depolymerization were identified as main reaction pathways occurring above 200°C.¹⁰ It has been revealed that CH groups of the main chain and the character of functional end groups primarily affect thermal and hydrolytic sensitivity of PLA.^{11,12}

There are a few strategies that can be used to improve thermal stability of PLA such as modification of functional groups during synthesis, copolymerization, crosslinking, blending with other polymers/copolymers, and introduction of fillers. Tan et al. increased the T50 (the temperature at which 50% weight loss occurs) of PLA by about 5°C–10°C by blending PLA with 3 wt % of poly(methyl methacrylate-co-glycidyl methacrylate) copolymer.¹³ Yang et al. increased the T50 of PLA by about 27°C by cross-linking with 3 wt % of triallyl isocyanurate and 1 wt % of dicumyl peroxide via reactive melt blending.¹⁴ Wu et al. reinforced PLA with 6 wt % of organically modified montmorillonite (m-MMT treated with n-hexadecyl trimethylammonium bromide and chitosan) by solution casting and thus increased the T50 by about 28°C.¹⁵ Kopinke et al. decreased thermal sensitivity of PLA by acetylation of its chain ends.¹⁶ Concerning thermal degradation of PLA, different degradation processes in nitrogen and oxygen were announced. During thermo-oxidative destruction of PLA were found acetaldehyde, lactide, carbon monoxide, and carbon dioxide as

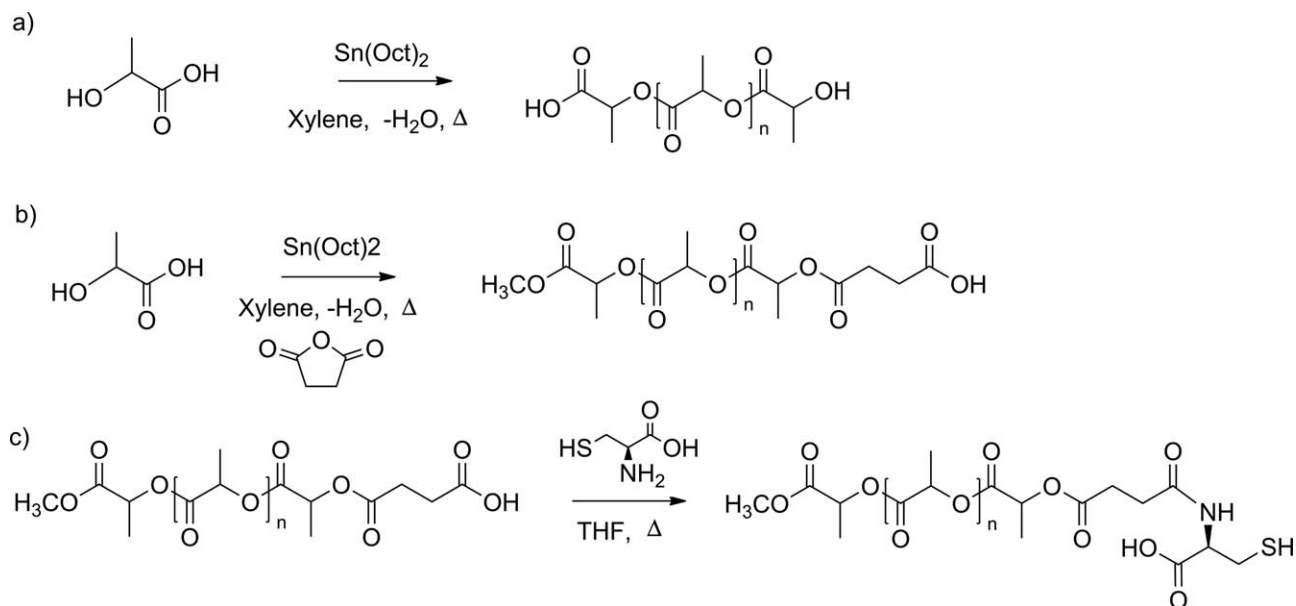


Figure 1. Syntheses scheme of (a) PLA, (b) PLA/SA, and (c) PLA/SA/CY.

products of decomposition, but in the nitrogen PLA decomposed in water, short-chain acids, carbon monoxide, and carbon dioxide.¹⁷

The aim of our work was to investigate the effects of functional end group modification on thermal stability of low molecular weight L-poly(lactic acid) (L-PLA). Thermal stability was determined by using thermogravimetric analyses (TGA) in nitrogen and oxygen atmospheres. The influence of the character of PLA end groups on the movement of the polymer chains in the transition region was investigated by dynamic mechanical analysis. As the mechanical loss factor value ($\tan \delta$) is independent of sample geometry, the application of a unique non-tensioning powder clamp embedded in a dual cantilever clamp enabled us to study viscoelastic properties of polymer samples without definite dimensions.

EXPERIMENTAL

Materials

L-Lactic acid, 80% aqueous solution of the monomer, 95% optically pure was purchased from Carl Roth (Austria). Tin (II) 2-ethylhexanoate, $\text{Sn}(\text{Oct})_2$ (95%), triethylamine (99%), succinic anhydride (99%), and L-cysteine (97%) were supplied by Sigma Aldrich (Germany) and 4-dimethylaminopyridine (99%) by Fluka. The solvents m-xylene (98.5%) from Carl Roth (Austria) and tetrahydrofuran from Sigma Aldrich (Germany) were purified by distillation. Chloroform (99%), n-Hexan (99%), and methanol (99.5%) were used as obtained from Carl Roth (Austria). For NMR spectroscopy, chloroform-d with TMS (0.03%) and deuteration degree of 99.96% from Sigma Aldrich (Germany) was used.

Synthesis of L-PLA Samples

The scheme for synthesis of neat PLA and PLA with modified functional end groups is shown in Figure 1.

Poly(lactic acid) (PLA). Azeotropic dehydration condensation was performed using a Dean–Stark apparatus in combination

with a reflux condenser and a 250 mL batch reactor for continuous removal of water. In the first step, 50 mL of 80% L-lactic acid was dehydrated in refluxing m-xylene for 4 h at 140°C, which collected about 14 mL of water. After dehydration, $\text{Sn}(\text{Oct})_2$ (0.5 wt % with respect to the mass of the dehydrated lactic acid) as catalyst was added and the azeotropic dehydration condensation was continued for 24 h at 200°C. At the end of the polymerization about 20 mL of water was collected and the residual m-xylene was removed from the reaction mixture, the reaction product was cooled to room temperature. The obtained polymer was purified via precipitation in n-Hexan. The precipitate obtained by filtration was dried in a vacuum, at 40°C for 48 h.

Poly(lactic acid) Modified with Succinic Anhydride (PLA/SA).

The dehydration step was the same as for the above-mentioned azeotropic dehydration condensation method of PLA. In the second step, 0.5 wt % of $\text{Sn}(\text{Oct})_2$, and 2.5 mol % of succinic anhydride (relative to the mass of the dehydrated lactic acid) were added and the azeotropic dehydration condensation continued for a further 24 h at 200°C. At the end of polymerization about 20 mL of water was collected and the residual m-xylene was removed from the reaction mixture. The purification and drying step were the same as for PLA synthesis.

Poly(lactic acid) Modified with Succinic Anhydride and L-Cysteine (PLA/SA/CY).

PLA/SA was dissolved in tetrahydrofuran, 2 mol % of L-cysteine, 0.06 mol % of 4-dimethylaminopyridine, and 0.12 mol % of triethylamine were added and the reaction was held at 80°C for 24 h. After the reaction, the solvent was removed completely and the polymer was purified by dissolving in chloroform and precipitated in chilled methanol. The powder obtained by filtration was dried in a vacuum at 40°C for 48 h.

Characterization of Samples

¹H Nuclear Magnetic Resonance (NMR). The structure of PLA polymers was analyzed by using a Bruker Avance III spectrometer operating at 300 MHz in a deuterated chloroform solution

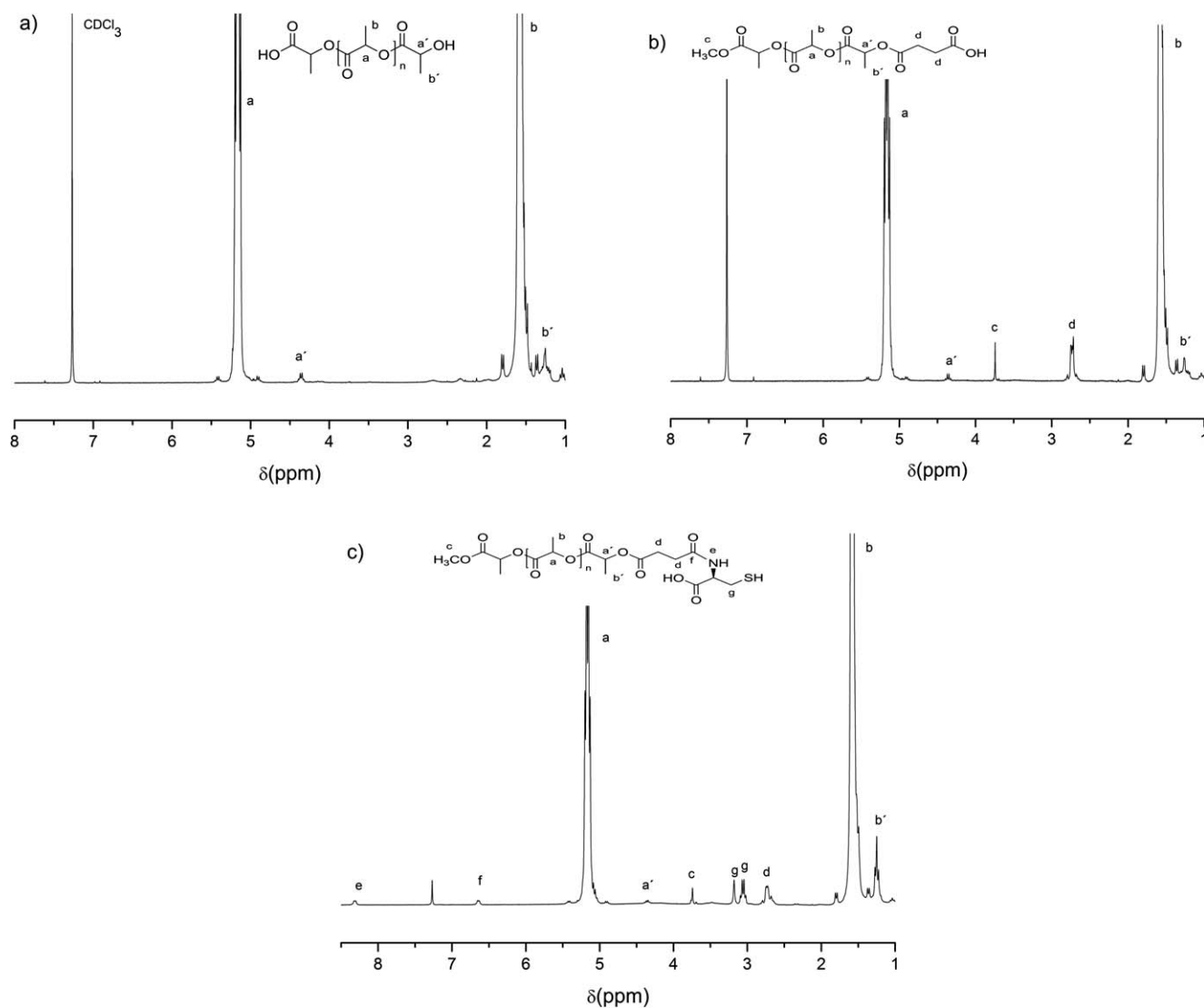


Figure 2. ^1H NMR spectra of (a) PLA, (b) PLA/SA, and (c) PLA/SA/CY.

with the TMS standard. All spectra were obtained at 25°C , 90° pulse angle, 5 s delay, and 64 scans.

Gel Permeation Chromatography (GPC). The average molecular weights (\overline{M}_n and \overline{M}_w), and the polydispersity PDI ($\overline{M}_w/\overline{M}_n$) were determined by gel permeation chromatography (GPC) instrument equipped with a L6000A Merck-Hitachi pump, a PPS sizing column ($5\ \mu\text{m}$, $8 \times 50\ \text{mm}$), two linear PL gel columns ($5\ \mu\text{m}$, $7.5 \times 300\ \text{mm}$) connected in series, and a Waters 410 differential refractometer. The columns were calibrated using narrow molecular weight polystyrene standards with molar mass ranging from 680 to 1,600,000 g/mol (Polymer

Standard Service). The samples were dissolved in chloroform at 4 mg/mL concentration and were analyzed at room temperature. Chloroform was used as an eluent at a flow rate of 1.0 mL/min and the injection volume was 100 μL .

Differential Scanning Calorimetry (DSC). Thermal properties of PLA samples were determined by using DSC Pyris Diamond Perkin Elmer at a constant heating rate of $10^\circ\text{C}/\text{min}$, nitrogen flow of 60 mL/min at the following heating program: running the first heating scan from 0°C to 170°C , holding for 1 min at 170°C , cooling to -20°C , holding for 1 min at -20°C , and running the second heating scan from -20°C to 170°C . Samples with a weight of approximately 5 mg were placed in alumina pans. Melting temperature (T_m) and enthalpy of melting (ΔH_m) were determined from the endothermic peaks (first heating scan). The glass transition temperature (T_g) was determined from the second heating scan as the midpoint stepwise increase of the specific heat.

Dynamic Mechanical Analysis (DMA). The viscoelastic properties of PLA samples in powder form were determined by using

Table I. GPC Characterization of PLA Polymers

Sample	\overline{M}_n	\overline{M}_w	PDI
PLA	21,400	35,600	1.7
PLA/SA	4,100	8,500	2.1
PLA/SA/CY	5,400	10,200	1.9

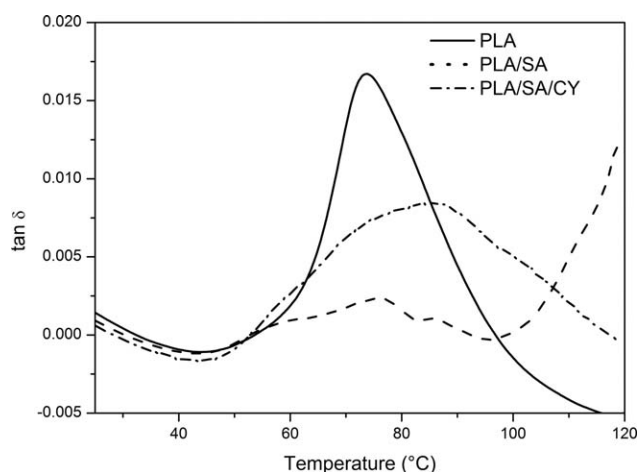
Table II. DSC Thermal Data of PLA Polymers Determined at a Heating Rate of 10°C/min

Sample	First heating scan				Second heating scan
	ΔH_{m1} (J/g)	T_{m1} (°C)	ΔH_{m2} (J/g)	T_{m2} (°C)	T_g (°C)
PLA	46	157	-	-	58
PLA/SA	29	145	-	-	52
PLA/SA/CY	43	151	87.8	220	57

a Dynamic Mechanical Analyzer DMA Q800, TA Instruments with application of non-tensioning powder holder embedded in a dual cantilever clamp. The powder holder was developed by Nick Hawkins.¹⁸ The mechanical loss factor values $\tan \delta = E''/E'$ and the glass transition temperature (T_g) determined as peaks of the $\tan \delta$ curves were measured for all samples by using the multifrequency strain mode at 1 Hz, the temperature scan from 20°C to 120°C, and the heating rate of 3°C/min. A sample of about approximately 300 mg was distributed uniformly in an aluminum powder holder with a size of 35 × 11.5 × 1.8 mm.

Thermogravimetric Analysis (TGA). TGA was performed using a STA-449C Netzsch analyzer. In the experiments, the samples (about 5 mg) were spread in perforated alumina crucibles. The following experimental setups were used to investigate thermal stability of PLA samples:

1. *Standard method*—a determination of sample weight loss in relation to a temperature area from 20°C to 550°C at a heating rate of 10°C/min, in a nitrogen and oxygen atmospheres with 50 mL/min nitrogen flow rate. Moreover, from the derivative thermogravimetric curve (DTG) was determined peak maximum temperature, T_{max} that corresponds to maximum decomposition rate.
2. *Determination of an activation energy*—an activation energy was calculated at each conversion rate α (in the range of 0.1–0.8 conversion) by application Flynn–Wall–Ozawa method:^{19–23}

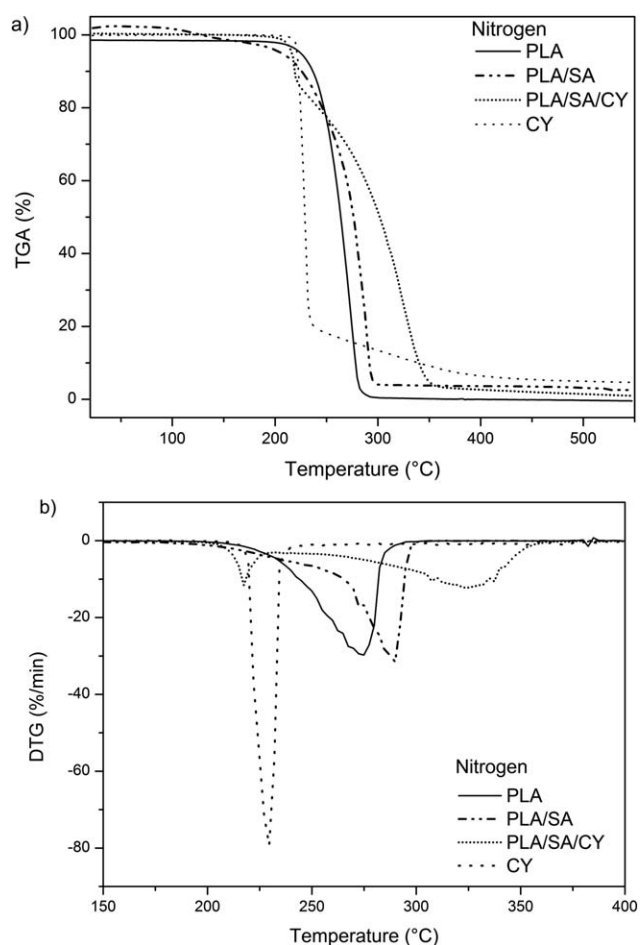
**Figure 3.** Temperature dependence of the mechanical loss factor of PLA samples.

$$\ln(\beta) = \left[A \frac{f(\alpha)}{d\alpha/dT} \right] - \frac{E_a}{RT} \quad (1)$$

where, β is a heating rate and α is a conversion rate. The experiments run in nitrogen and oxygen atmosphere (50 mL/min flow

Table III. Mechanical Loss Factor ($\tan \delta$) Data Determined by DMA Using the Powder Holder

Sample	$\tan \delta$ (°C)	$\tan \delta$ height	$\tan \delta$ full-width-at-half-maximum (°C)
PLA	73.8	0.020	21.3
PLA/SA	75.7	0.004	23.8
PLA/SA/CY	84.5	0.009	41.3

**Figure 4.** TGA (a) and DTG (b) curves of PLA samples and L-cysteine (CY) in nitrogen.

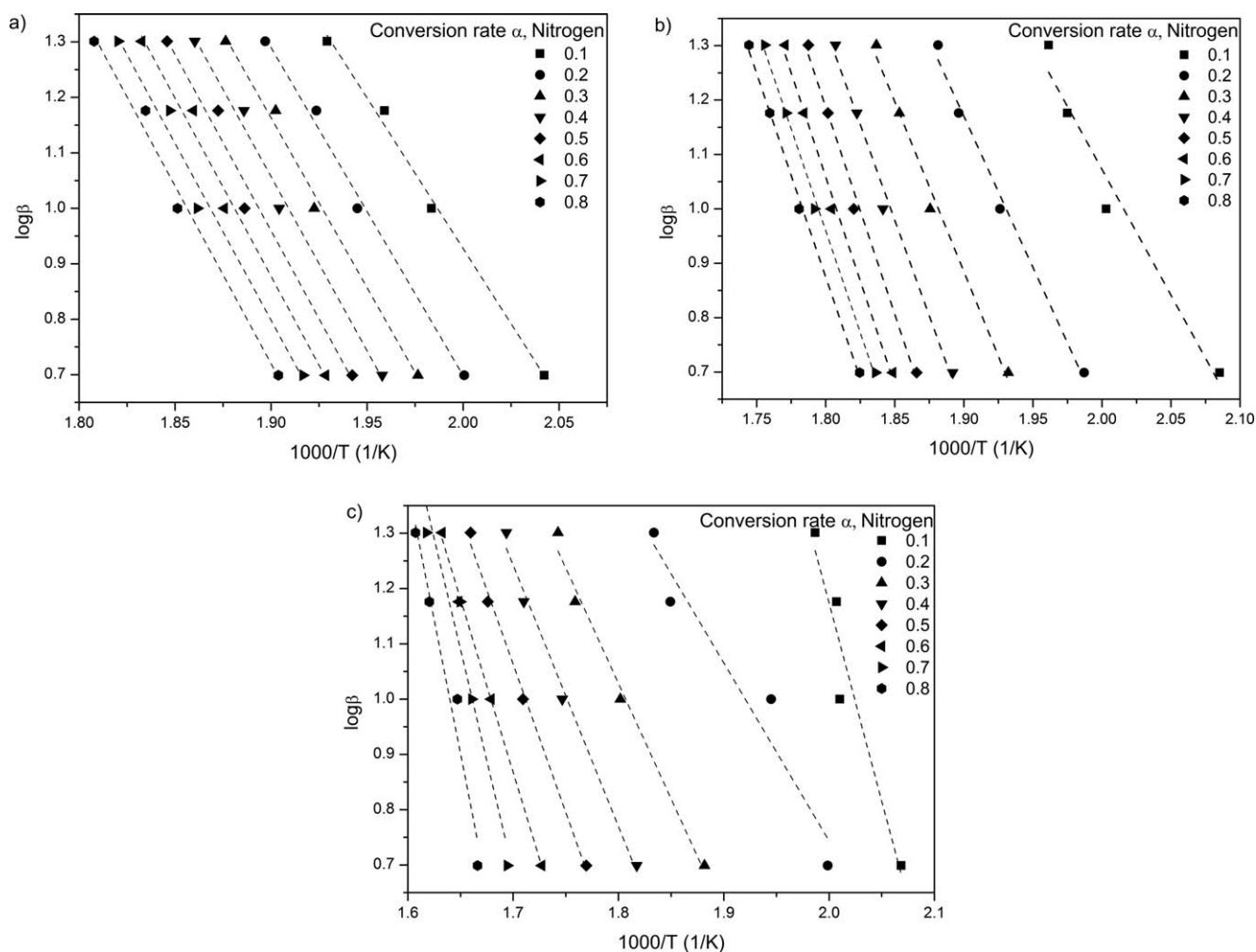


Figure 5. Iso-conversional plots of Flynn–Wall–Ozawa method in nitrogen of (a) PLA, (b) PLA/SA, and (c) PLA/SA/CY

rate) from 20°C to 550°C, at multiple heating rates of 5°C/min, 10°C/min, 15°C/min, and 20°C/min.

3. *Isothermal thermo-oxidation degradation*—an investigation of weight changes in relation to retention of sample at determined critical onset degradation temperature (250°C) in an

oxygen atmosphere (50 mL/min flow rate). At first, the heating scan from 20°C to 250°C with a 50°C/min heating rate, and after that, the isothermal scan at 250°C for 1 h were applied.

Table IV. Activation Energies of PLA Polymers Determined According Flynn–Wall–Ozawa Method in Nitrogen

Conversion rate α	Activation energy E_a (kJ/mol)		
	PLA	PLA/SA	PLA/SA/CY
0.1	99	84	136
0.2	108	101	63
0.3	112	114	76
0.4	115	128	86
0.5	116	139	98
0.6	117	140	117
0.7	116	136	146
0.8	117	136	177

RESULTS AND DISCUSSION

All synthesized polymers were white homogenous powders without smell. The ^1H NMR spectra of PLA polymers are shown in Figure 2. The characteristic methine and methyl chemical resonance of PLA were observed at 5.17 and 1.58 ppm, respectively [see Figure 2(a)]. Integration of (q, $-\text{CH}$ and d, $-\text{CH}_3$) peaks showed an approximate ratio of 1 : 3. The resonance at 4.36 ppm (q, $-\text{CH}$), 3.74 ppm (s, $-\text{OCH}_3$), and 1.25 ppm (br, $-\text{CH}_3$) originates from lactyl unit end groups. Figure 2(b) shows PLA/SA sample with the resonance of succinic anhydride end capping groups at 2.73 ppm (br, $-\text{CH}_2$). The coupling of L-cysteine with PLA via peptide bond can be shown in Figure 2(c).

PLA polymers were characterized by GPC in chloroform and the molecular weights are listed in Table I. The determined low molecular weights ($\overline{M}_n = 4100$, $\overline{M}_w = 8500$) of the polymer-

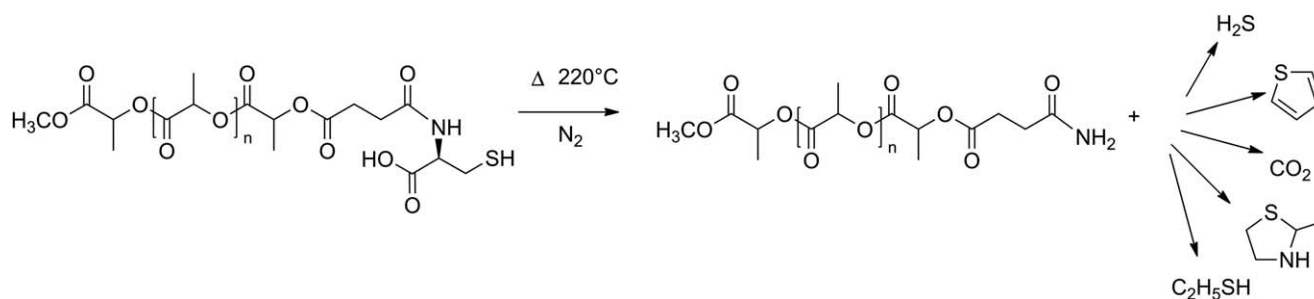


Figure 6. Proposed mechanism of thermal degradation of the PLA/SA/CY sample in nitrogen at 220°C.

capped carboxyl end groups (PLA/SA) proved the rule that the use of difunctional additive during polymerization decreases the molecular weight of a polymer. Further modification of PLA/SA with L-cysteine slightly increased the resulted molecular weights ($\overline{M}_n = 5400$, $\overline{M}_w = 10,200$) of such functionalized PLA (PLA/SA/CY).

DSC and DMA analyses were used to characterize the effect of functional end groups on thermal properties of PLA samples. DSC data proved semi-crystalline character of the synthesized PLA samples (Table II). The value of T_g is dependent on various factors such as molecular weight of polymer, presence of mois-

ture, presence of the crystalline phase (in the case of semicrystalline polymers). DSC data shows that the different molecular weights of PLA samples affected their glass transition and melting temperatures. However, it can be seen that also the character of their functional end groups influenced their resulted thermal properties considerably. All modified PLA samples showed the decrease of melting enthalpy and melting peak temperature values that indicate the modification of crystalline regions. Neat PLA was characterized by T_g of 58°C, T_m of 157°C, and a crystallinity of 48.9%. All modified PLA samples exhibited decrease in crystallinity in comparison to the neat PLA; however, the decrease of crystallinity for PLA/SA/CY was not so substantial.

The application of the non-tensioning powder clamp embedded in a dual cantilever clamp enabled us to determine damping properties of the synthesized PLA samples in powder form. It is important to notice that the T_g value determined by DMA as the peak maximum of $\tan \delta$ curve can shift about 20°C to higher temperatures in comparison to the T_g determined by DSC due to the other kind of the determination methodology and process. Figure 3 shows $\tan \delta$ curves of the PLA sample influenced by the type of functional end groups and molecular weight. The height and the shape of the $\tan \delta$ peak depend on the polymer chain's entanglement and the resulting polymer chain's movement. The values of peak temperatures, heights of the $\tan \delta$ peaks, and the corresponding full-width-at-half-maximum values are given in Table III. The $\tan \delta$ peak heights of samples with modified functional end groups were lower than those of the neat PLA due to the restriction of movement of the polymer molecules. The glass transition of neat PLA and PLA with modified functional end groups occurs of about 73.8°C–84.5°C. T_g values taken as the $\tan \delta$ peaks and the values of the corresponding full-width-at-half-maximum values of PLA and PLA/SA were nearly identical, with the exception of the PLA/SA/CY values. The shift of the T_g value of PLA/SA/CY by 10.7°C in comparison to that of neat PLA relates to the reduced mobility of macromolecules due to the new functional end groups. The broadening of full-width-at-half-maximum values indicates the changes to the polymer chain movement due to the different molecular relaxations.

Thermal degradation behavior of PLA polymers was investigated by TGA in a nitrogen and oxygen atmospheres. Figure 4 shows the TGA and DTG curves of PLA samples and L-cysteine determined in nitrogen atmosphere. The weight loss of neat PLA in nitrogen started smoothly at around 221°C and reached T_{max}

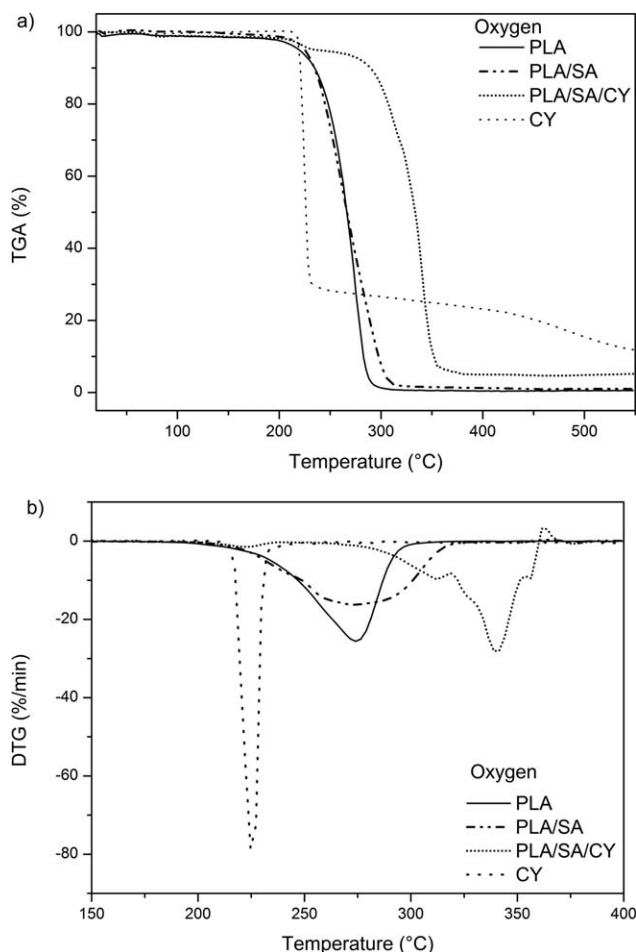


Figure 7. TGA (a) and DTG (b) curves of PLA samples and L-cysteine (CY) in oxygen.

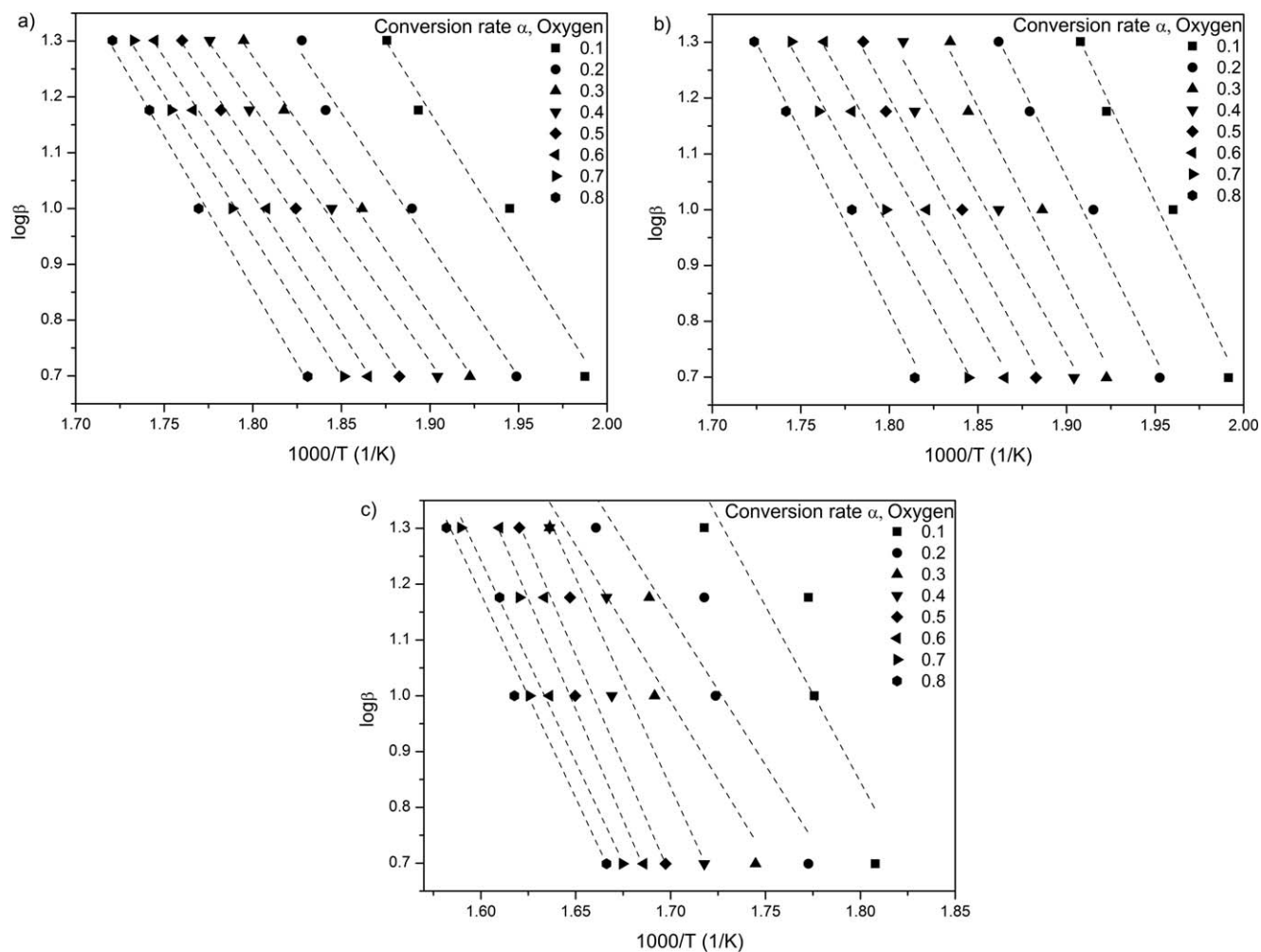


Figure 8. Iso-conversional plots of Flynn–Wall–Ozawa method in oxygen of (a) PLA, (b) PLA/SA, and (c) PLA/SA/CY.

(degradation temperature with the highest decomposition rate) at 270°C. PLA/SA and PLA/SA/CY started to decompose in nitrogen slightly earlier than neat PLA but reached higher T_{max} values, about 15°C and 60°C, respectively. PLA/SA/CY shows two visible weight loss peaks at 220°C and 330°C. The first peak is similar

to L-cysteine weight loss peak and the second peak represents the decomposition of the modified PLA. The thermal stability of PLA modified with succinic anhydride and L-cysteine was

Table V. Activation Energies of PLA Polymers Determined According Flynn–Wall–Ozawa Method in Oxygen

Conversion rate α	Activation energy E_a (kJ/mol)		
	PLA	PLA/SA	PLA/SA/CY
0.1	93	125	115
0.2	86	117	98
0.3	85	116	102
0.4	84	104	137
0.5	88	107	144
0.6	90	103	145
0.7	92	107	132
0.8	99	117	133

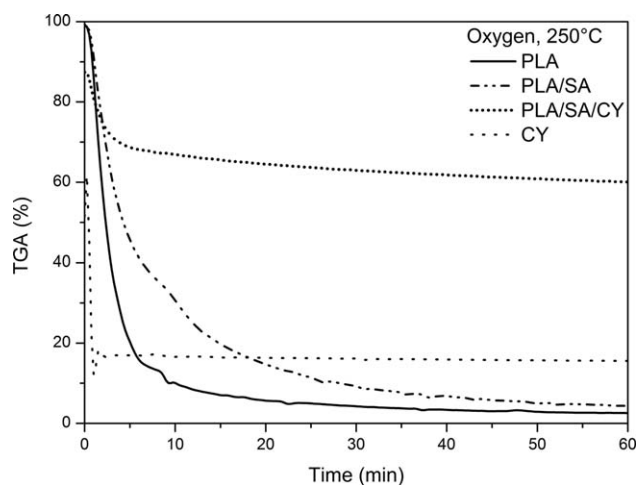


Figure 9. Weight losses of PLA samples and L-cysteine (CY) at 250°C in oxygen.

Table VI. Thermal Stability Data of PLA Polymers and L-Cysteine (CY) Determined in O₂, at 250°C for 1 h

Sample	Weight loss (%) after time		
	10 min	30 min	60 min
PLA	90.1	95.8	97.5
PLA/SA	69.4	90.8	95.6
PLA/SA/CY	33.1	37.0	40
L-cysteine	83.4	83.9	84.5

additionally analyzed by a determination of an activation energy, using Flynn–Wall–Ozawa method. Flynn–Wall–Ozawa method was proved as an successful model-free method to simulate multistep decomposition kinetic.^{21,23} Figure 5 and Table IV represent iso-conversional decomposition plots and values of activation energies in nitrogen of PLA samples based on Flynn–Wall–Ozawa method. The neat PLA showed in nitrogen parallel lines in the conversion range of 0.1–0.8, which indicates the single reaction mechanism during thermal degradation at a corresponding temperature range of 216°C–280°C. The decomposition of PLA/SA in the range of $\alpha = 0.1$ –0.3 was similar to that of neat PLA, while at the conversion rate higher than 0.3 were the values of activation energies much higher. PLA/SA/CY showed a complex decomposition mechanism. The activation energy of PLA/SA/CY at the conversion rate of $\alpha = 0.1$ was about 37% higher than that of the neat PLA. However, the value of E_a at the conversion rate of 0.2 drastically decreased from 136 to 63 kJ/mol. Further, the values of activation energy in the conversion range of 0.3–0.8 gradually increased to 177 kJ/mol. The alteration of the decomposition mechanisms during the change of the conversion rate indicates the multiple cleavage reaction mechanism. It is seen that the amino end group, remaining after the decomposition of L-cysteine ions from PLA/SA/CY (Figure 6), could increase the thermal stability of PLA in nitrogen only at very low or very high conversion periods. Yablokov et al. reported that thermal decomposition of L-cysteine consists from a few parallel and consecutive radical reactions with cleavage of the C–C and the C–S bonds but with the exception of the C–N bond.²⁴ It was detected that the decomposition of L-cysteine was accompanied by evolution of H₂S, C₄H₄S, CO₂, C₄H₉NS, and C₂H₅SH.²⁴

Figure 7 shows TGA and DTG curves of PLA samples in oxygen atmosphere. The decomposition pattern of neat PLA in oxygen was similar to that in the inert atmosphere. However, the thermal decomposition of the modified PLA/SA in oxygen began earlier about 9°C than in nitrogen. The value of the second DTG weight loss peak of PLA/SA/CY was shifted to the higher temperature in the comparison to nitrogen atmosphere. The thermal stability of PLA samples in oxygen based on the standard thermogravimetric analysis at heating rate of 10°C/min can be ordered as PLA < PLA/SA < PLA/SA/CY. Moreover, the iso-conversional plots and activation energy's values describing thermal degradation of PLA samples in oxygen are displayed in Figure 8 and Table V. The evaluated values of activation energies based on Flynn–Wall–Ozawa method indicate different kind of degradation mechanism resulting in a lower thermal stability of modified PLA samples in oxygen comparing to that in the inert atmosphere. Furthermore, a thermo-oxidative stability of PLA samples was determined under isothermal conditions (see Figure 9). Table VI displays the determined values of weight loss for all PLA samples in oxygen at the temperature of 250°C and the exposition time of 60 min. The modification of functional groups decreased the sensitivity of PLA to thermo-oxidative degradation at 250°C. The PLA/SA/CY sample exhibited the highest thermal stability under isothermal thermo-oxidative conditions, with the improvement about 57% in comparison to neat PLA. The suggested mechanism of the structure change of PLA/SA/CY under the thermo-oxidative degradation is given in Figure 10. A similar mechanism was proposed for L-cysteine containing peptides by Basile et al.²⁵ Determination of the effect of time on the stability of the PLA samples at isothermal thermo-oxidative conditions (250°C, oxygen atmosphere, isotherm for 1 h) showed 50% weight loss of the sample after 12.4–14.3 min for the tested samples with the exception of PLA/SA/CY, which presented 60.1% of its original weight even after 1 h.

CONCLUSIONS

L-PLA polymers with various functional end groups were synthesized by azeotropic dehydration condensation. The presented study showed that the transformation of hydroxyl end groups to carboxyl and amino end groups during synthesis can mildly change thermal stability of low molecular weight PLA. The apparent activation energies of thermo-decomposition for the

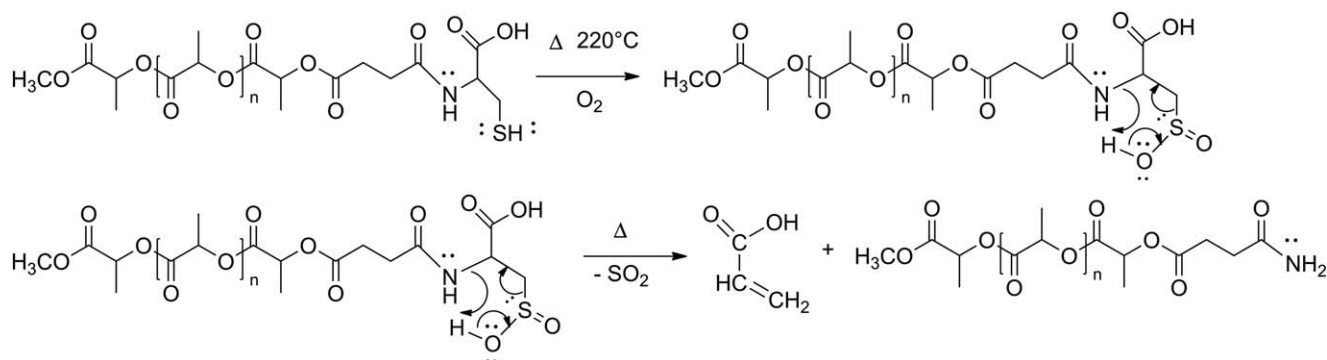


Figure 10. Proposed mechanism of thermal degradation of the PLA/SA/CY sample in oxygen at 220°C.

PLA samples in nitrogen as well as in oxygen atmospheres increased in the order of PLA < PLA/SA < PLA/SA/CY. PLA/SA/CY polymer showed the highest stability under isothermal and non-isothermal thermo-oxidative conditions due to the presence of amino end groups.

Moreover, the effect of modified end-capped PLA on its thermal and viscoelastic properties was investigated by DSC and DMA analyses. The determined differences in melting behavior and mechanical loss factor peak position endorsed the dependence of thermal and damping properties of PLA on its functional end groups.

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