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Study of Thermodegradation and Thermostabilization of Poly(lactide acid) Using Subsequent Extrusion Cycles

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ABSTRACT: The thermomechanical degradation and thermostabilization of poly(lactic acid) (PLA) have been studied using subsequent extrusion cycles under different temperature profiles. Primary and secondary antioxidants were used to avoid degradation process during extrusion. Melt flow index (MFI), size exclusion chromatography (SEC), and infrared spectroscopy (FTIR) analysis were used to evaluate the degradation and stabilization of PLA. The MFI and SEC analysis show that the main thermodegradation mechanism of PLA is governed by scission reactions. FTIR analysis confirmed the SEC results and showed that the synergetic effect between primary and secondary antioxidant is a suitable way to thermostabilize the PLA. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40023.

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INTRODUCTION

In the search for new solutions as an alternative to replace conventional polymers, the use of the biodegradable polymers has achieved a prominent position.[1–4] Thus, the researches about these materials have also gained increasing proportions.[5–10] However, mechanical and thermal properties of some biodegradable polymers are still bellow of conventional polymers and they also show a lower thermostability during the processing. These factors led to a low demand of the biodegradable polymers on the world market.[11] Another important aspect is that the world community has in mind that products made from biodegradable polymers must have a short useful life and they could not be recycled.[12,13] Furthermore, oil is the most widely used raw material for producing plastic (nonrenewable) and in the case of biodegradable polymers this source could be replaced by a renewable source.

Nowadays, the general population, the academic community and the industry are adapting to biodegradable plastics (production and use), besides reviewing the concepts related to them. In the very near future the presence of biodegradable polymers cannot be just a way to reduce the accumulation plastic in landfills, but it could be also an alternative to replacement of conventional polymers.

From the foregoing, it is noted that there is a large field to be explored in the area of biodegradable polymers. Biodegradable polymers could be used and sometimes their biodegradability could not be triggered, leading to the need to add stabilizing additives to increase its lifetime. That is similar to what happens with conventional polymers. Also because of that, mechanical recycling process becomes possible without major damage in its properties. The recycling of polymers is a way to maintain the energy contained in polymers (raw material, synthesis, and processing) without being wasted after only one use. The biodegradability of these polymers is only triggered when they are properly disposed in appropriate locations.

Biodegradable polymers can be classified simplify as natural or synthetic. So called "natural polymers" are formed during the growth cycle of living organisms. Its synthesis generally involves enzyme-catalyzed reactions and reactions of chain growth from activated monomers, which are formed inside the cells by complex metabolic. Starch, cellulose, chitosan, and polyhydroxyalkanoats (PHA) are examples of natural biodegradable polymers. Poly(ε-caprolactone) (PCL) and poly(lactic acid) (PLA) are two types of synthetic biodegradable polymers.[3] The monomer to produce PLA, lactic acid, can be manufactured either by carbohydrate fermentation or chemical synthesis, although fermentation predominates.[14] PLA is the most used biodegradable polymer in the world.[11] The biodegradability of PLA is directly related to the presence of the ester group which is easily hydrolyzed. This hydrolysis reaction leads to reduction of molecular weight, which occurs mainly through the action of esterase

Table I. Stabilizers Used and Their Concentrations

Stabilizer	Concentrations (w/w)
Irganox 1010	0.5
Irganox 1076	0.4
Irgafos 168	0.8
Irganox B900[a]	0.2

[a] Irganox B900 is a synergistic blend of IRGAFOS 168 (80%) and IRGANOX 1076 (20%).

enzymes that are easily found in soil. The synthesis of PLA with high molecular weight was described by Carothers et al. in 1932. Since 1970, copolymers based on lactic and glycolic acids are used in biomedical applications, such as degradable matrix for the controlled release of drugs.[15,16] However, the same ester group responsible for the biodegradability is also a vulnerable linkage for thermodegradation during the processing. The thermodegradation leads to decreasing of molecular weight, consequently there are mechanical properties loss and coloration changes.

The first proposal of this work is evaluating the thermomechanical degradation of PLA using subsequent extrusion cycles under different temperature profiles. The second step intends to evaluate the efficiency of some thermal stabilizers (primary and secondary antioxidants) during the subsequent extrusion cycles at highest temperatures. After each extrusion cycle an amount of the sample was collected to posterior analysis. Melt flow index (MFI) analysis, size exclusion chromatography (SEC), and infrared spectroscopy (FTIR) analysis were used to evaluate the degradation of PLA during extrusion process. It is expected that the results lead to a possibility of thermostabilization of PLA and thus guarantee the possibility of re-using and recycling of PLA.

EXPERIMENTAL

Materials

In this work, commercial PLA—from Cargill (MFI = 10.5 g/10 min, 190°C/2.16 kg) was used. The stabilizers and the concentrations used in this work are presented in Table I. The structures and chemical names of the additives are in Scheme 1. The stabilizer concentrations were chosen according to the commercial data sheet of these additives.

Master-Batch Preparation

As the concentrations of additives are very low, it was preferred to prepare master-batches with a percentage of 10% by weight of additive in the PLA. After that a fresh mixture with pure PLA and master-batch was made to achieve desired concentrations. The preparation of the concentrates was carried out in a mechanical mixer and then they were cut into a knife mill to obtain smaller sizes.

Thermodegradation

The thermomechanical degradation was performed on a rheometer coupled to a single-screw extruder (Haake Fisions Rheodrive 5000). In the first step, subsequent extrusions were performed with no additive PLA using different temperature profiles. The temperature profiles are presented below:

1. 170, 180, 190, and 210°C;
2. 180, 190, 200, and 220°C;
3. 190, 200, 210, and 230°C.

It was performed five subsequent extrusion cycles at each temperature profile. A rotation speed equal to 60 rpm was maintained during all cycles. Initially and between cycles, the PLA was dried in an oven for 1 h at 100°C. The same procedure was used for PLA + stabilizers. This procedure is indicated by the supplier to prevent hydrolysis of PLA during the extrusion process, since this polymer is very hygroscopic.

Characterization

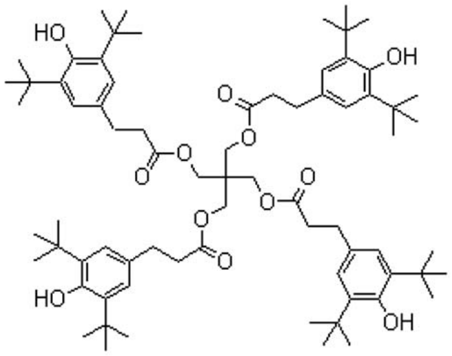
After inducing the neat PLA to thermomechanical degradation, the degradation was monitored by measurements of MFI. The tests were performed on a Tinius Olsen Plastometer, using temperature of 190°C and a weight of 2.16 kg. The drying process was also maintained before the analysis.

After the study with neat PLA, the subsequent extrusion cycles with the addition of stabilizers were initiated. The temperature Profile 3 was chosen for this study because the results of MFI showed a high level of degradation of PLA (as will be seen on the Results). At this second step, the monitoring of the degradation process was more specific. Beyond the analysis of MFI, SEC and FTIR analyses were also performed. SEC analyses were conducted in a Viscoteck with a series of columns at 40°C and with a refractive index detector. Specimens were dissolved in tetrahydrofuran (THF) and the filtered solution was injected into the equipment. The solvent flow rate (THF) was 1 mL/min and the columns were calibrated with narrow molecular weight PS. Infrared analyzes were performed to analyze difference in the chemical structure of the PLA when submitted to subsequent extrusion cycles with and without additive stabilizers. To perform the FTIR analysis, a small fraction of each sample (4 mg) was dissolved in 4 mL of tetrahydrofuran (THF), the solution was transferred to Petri dishes and after solvent evaporation, and a thin film was obtained. The FTIR samplings by transmission analyses were performed on a Perkin Elmer spectrophotometer between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1}. The FTIR spectra were analyzed based on the ratio of the band intensity and an internal standard band of PLA film, in this case at 1454 cm^{-1} (CH_2 deformation).[17] Furthermore, deconvolution curves (Lorentzian mode) were drawn to confirm the band's maxima.

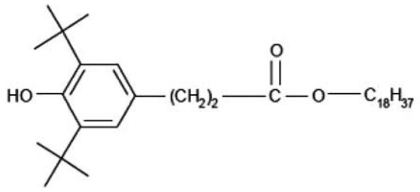
RESULTS AND DISCUSSION

Thermodegradation of Neat PLA—MFI

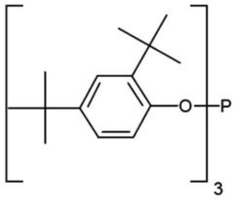
In preliminary studies, only MFI data were used to infer the mechanism of thermal degradation of the neat PLA. MFI of the neat PLA was obtained in previous tests and the results was 10.88 ± 0.54 g/10 min. Table II shows the MFI results for neat PLA after five subsequent extrusion cycles with the temperature Profiles 1, 2, and 3. In this same table, the results show that the increasing of extrusion cycles also leads a slight increasing in the MFI values. This indicates that the thermodegradation



Irganox 1010 - Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)



Irganox 1076 - Octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate



Irgafos 168 - Tris (2,4-di-tert-butylphenyl)phosphite

Irganox B900 - Blend of IRGAFOS 168 (80%) and IRGANOX 1076 (20%).

Scheme 1. Stabilizers' molecular structures.

process of PLA has scission molecular reactions as main route. This effect was greater for the temperature Profile 3, indicating also the strong influence of temperature on the degradation mechanism. The MFI increase after five extrusion cycles using temperature Profile 3 was about 57.6%.

Thermodegradation of PLA + Stabilizers—MFI and SEC

After the previous results, the temperature Profile 3 was chosen for studying the efficiency of stabilizing additives, since this profile was the most aggressive. Initially, the MFI measures were used to evaluate the efficiency of additives. Table III shows the MFI values for PLA + stabilizers submitted to five subsequent extrusion cycles. In Table III, the MFI values after five cycles of extrusion are higher than neat PLA submitted to the same conditions. An explanation for this characteristic is the fact that samples with stabilizer are a mix of neat PLA and master-batch. This master-batch has already been exposed to high temperature during its production and the molecular weight was decreased. Figure 1 shows the molecular weight distribution curves of neat PLA and the master-batch. As seen in Figure 1, the molecular weight distribution curve of master-batch (PLA + 10% of Irganox 1010) shows a low molecular weight peak that cannot be observed on neat PLA curve. Probably, this peak is a product of PLA degradation that occurred during the master-batch preparation. Another phenomenon to explain these results was already clarified by Fechine and coworkers.[18] This can be explained by the thermodegradation that occurs during the MFI measurements. The MFI analysis is done at high temperatures and under shear stress. At the beginning of the test, the sample is submitted to high temperatures for some time (typically 6–7 min) before analysis to reach thermal equilibrium. Normally, during the MFI analysis occurs a thermodegradation *in situ*. This process is faster for samples already exposed to high temperature as PLA + stabilizer than for neat PLA. However, the initial values for all samples are different, and only the percentage of increasing has to be taken into consideration. After five cycles, the samples of PLA + stabilizers showed an increasing of 43.6, 57.6, 74.8, and 69.1% for samples with Irganox 1010, Irganox 1076, Irgafos 168, and Irganox B900, respectively. In this case, Irganox 1010 showed better results, since the increase in

Table II. MFI Results (g/10 min) for Neat PLA Submitted to Subsequent Extrusion Cycles at Different Temperature Profiles

Extrusion cycles	Profile 1	Profile 2	Profile 3
1	11.22 ± 0.22	12.13 ± 0.40	10.82 ± 0.64
2	12.15 ± 0.22	11.85 ± 0.30	12.00 ± 0.39
3	13.28 ± 0.48	12.90 ± 0.47	13.78 ± 0.33
4	14.08 ± 0.56	14.32 ± 0.34	14.56 ± 0.63
5	15.18 ± 0.61	16.85 ± 1.44	17.05 ± 0.58

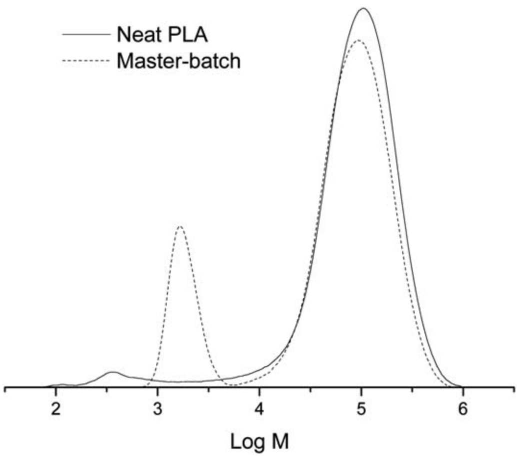


Figure 1. Molecular weight distribution curves of neat PLA and master-batch (PLA + 10% of Irganox 1010) samples.

MFI values compared to the other samples containing the stabilizer was the smallest. Nevertheless, measures of MFI are not so enlightening; they could give only an "indication" of molecular weight variations. The results obtained by SEC will be more realistic.

Table IV shows the SEC results for the neat PLA processed in the temperature Profile 3. MFI results presented for neat PLA using temperature Profile 3 showed that there is an increase of the values with the number of extrusion cycles. The molecular weights data shows that the increase of number of extrusion cycles lead to a variation of molecular weight, $\overline{M}_n$ and $\overline{M}_w$. As said before, the MFI results just give an "indication" about the molecular weight and the SEC results always are more precise. The values of $\overline{M}_n$ and $\overline{M}_w$ increased and the polydispersity (PD) decreased after first extrusion, indicating a considerable number of crosslinking reactions. After three cycles, the molecular weights started to decrease and the PD increased in relation to the first cycle. In this case, the scissions reactions started to be more pronounced. At the end of five cycles, the molecular weight dropped further and the PD reached 1.94, indicating that five cycles is a good choice to evaluate the thermostabilization of PLA. All these results can also be easily observed through the molecular weight distribution curves. Figure 2 shows the curves for neat PLA processed with the temperature Profile 3. Clearly, it is verified that the molecular weight curves are displaced to lower molecular weight after five extrusion cycles.

Table V presents the SEC results of PLA + stabilizers processed in the temperature Profile 3 after five subsequent extrusion cycles. Data from neat PLA and PLA + stabilizers after five cycles of extrusion show that Irganox 1010 and Irganox B900 induce a retardant effect into PLA thermodegradation. The PD of these samples also indicates this phenomenon since the values of PD (1.85 and 1.87, Irganox 1010 and B900, respectively) remain almost the same as neat PLA without being processed (1.84). Between these two stabilizers, Irganox 1010 e B900, the last one presented the best results. An explanation for that is that the formulation of Irganox B900 is a synergetic blend formed by Irganox 1076 (primary antioxidant) and Irgafos 168 (secondary antioxidant). Primary antioxidants are generally radical scavengers or H-donors and secondary ones are typically hydroperoxide decomposers. Consequently, Irganox B900 retards the thermodegradation of PLA during the extrusion process by two different ways meanwhile the other stabilizers act by one way. This result could also be seen in Figure 3 that shows the molecular weight distribution curves for neat PLA and PLA + stabilizers processed in the temperature Profile 3 after five extrusion cycles. Even taking into account the errors associated with SEC measurements, among all of the samples it is noticed that PLA+ B900 after five cycles showed higher values of $\overline{M}_n$ and $\overline{M}_w$, and also a distribution of molecular weight near to neat PLA.

Nevertheless, some questions remain: Why the efficiency of additives was not good as expected? Why the additives 1076 and 168 confer a good stabilizing effect to the PLA? The answers for those questions could be explained with chemical modification analysis.

Chemical Modifications

During the thermodegradation process of many polymers scission reactions and/or crosslinking can occur and new chemical

Table III. MFI Results (g/10 min) for PLA + Stabilizers Submitted to Subsequent Extrusion Cycles at Different Temperature Profiles

Extrusion cycles	Irganox 1010	Irganox 1076	Irgafos 168	Irganox B900
Before extrusion	12.21 ± 0.22	12.18 ± 0.76	11.17 ± 0.21	11.55 ± 0.63
1	12.50 ± 0.44	12.78 ± 0.39	12.97 ± 0.44	12.97 ± 0.55
2	14.42 ± 0.73	16.52 ± 0.81	14.22 ± 0.87	14.22 ± 0.65
3	15.37 ± 0.91	16.93 ± 1.59	17.04 ± 0.23	17.04 ± 0.82
4	15.97 ± 0.38	18.42 ± 0.57	17.70 ± 1.15	17.70 ± 0.75
5	17.53 ± 0.62	19.22 ± 1.23	19.53 ± 1.07	19.53 ± 0.54

Table IV. SEC Results for Neat PLA Submitted to Subsequent Extrusion Cycles at Temperature Profile 3

Extrusion cycles	$\overline{M}_n$	$\overline{M}_w$	PD
0	70,700	130,600	1.84
1	74,800	135,600	1.81
3	71,200	134,400	1.89
5	61,700	129,800	2.10

Table V. SEC Results for PLA + Stabilizer Submitted to Subsequent Extrusion Cycles at Temperature Profile 3

Stabilizer	$\overline{M}_n$	$\overline{M}_w$	PD
Irganox 1010	63,500	117,500	1.85
Irganox 1076	58,300	115,300	1.93
Irgafos 168	61,500	118,700	1.93
B 900	66,500	124,800	1.87

groups are generated.[19] Infrared spectroscopy analysis was performed to evaluate the chemical modifications occurred in the PLA during extrusion process.

The FTIR spectra of nonstabilized PLA and stabilized PLA submitted to subsequent extrusion cycles are presented in Figures 4 and 5, respectively. These spectra show some labeled bands which underwent modification after the extrusion cycles. Two bands are attributed to asymmetric vibration of the ester group (1092 and 1185 cm^{-1}). Another one is attributed to the carbonyl stretching (1758 cm^{-1}) and the last one attributed to CH_2 deformation is used as internal standard band at 1455 cm^{-1}.[17] As mentioned before all of the bands were normalized by the ratio of the each band intensity and the internal standard band. Table VI shows the variation on intensity of the ratios of

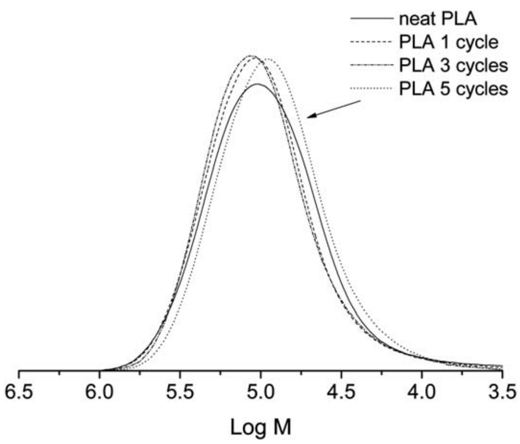


Figure 2. Molecular weight distribution curves of neat PLA and PLA submitted to one, three, and five cycles of extrusion.

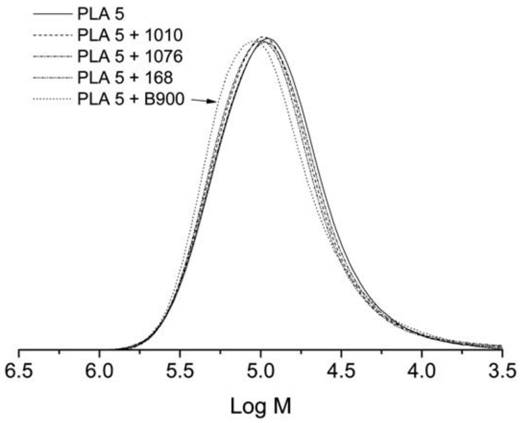


Figure 3. Molecular weight distribution curves of PLA, PLA + Irganox 1010, PLA + Irganox 1076, PLA + Irgafos 168, and PLA + B 900 submitted to five cycles of extrusion.

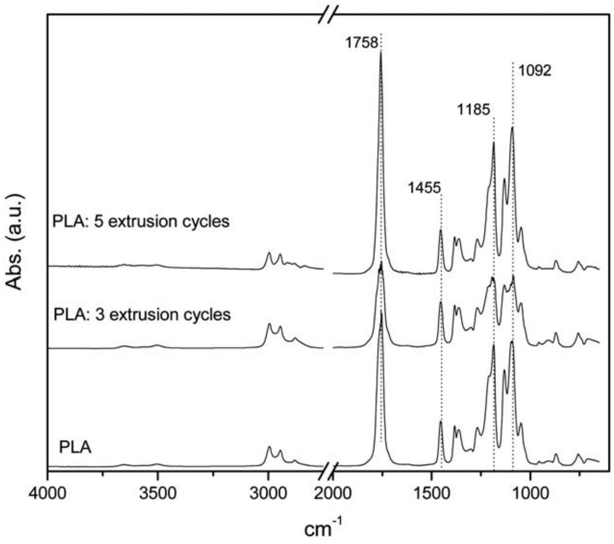


Figure 4. FTIR spectra of neat PLA and PLA submitted to one, three, and five cycles of extrusion.

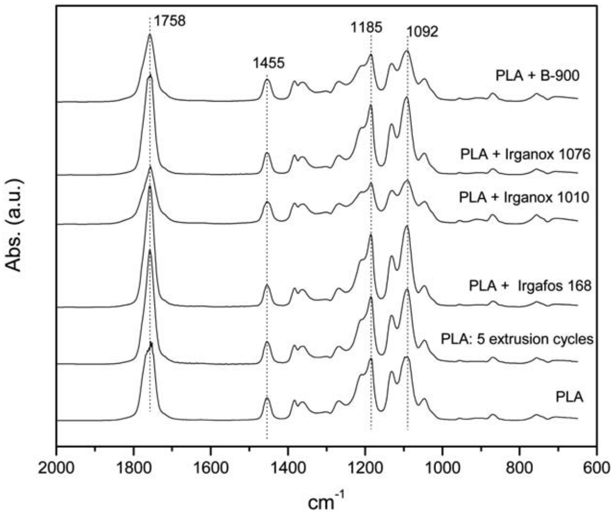


Figure 5. FTIR spectra of neat PLA and PLA, PLA + Irganox 1010, PLA + Irganox 1076, PLA + Irgafos 168, and PLA + B 900 submitted to five cycles of extrusion.

Table VI. Variation on Intensity of the Ratios of Three Bands, 1758, 1185, and 1092 cm^{-1}, of PLA Submitted to 3 and 5 Extrusion Cycles and PLA + Irganox 1010, PLA + Irganox 1076, PLA + Irgafos 168, and PLA + B 900 Submitted to Five Cycles of Extrusion

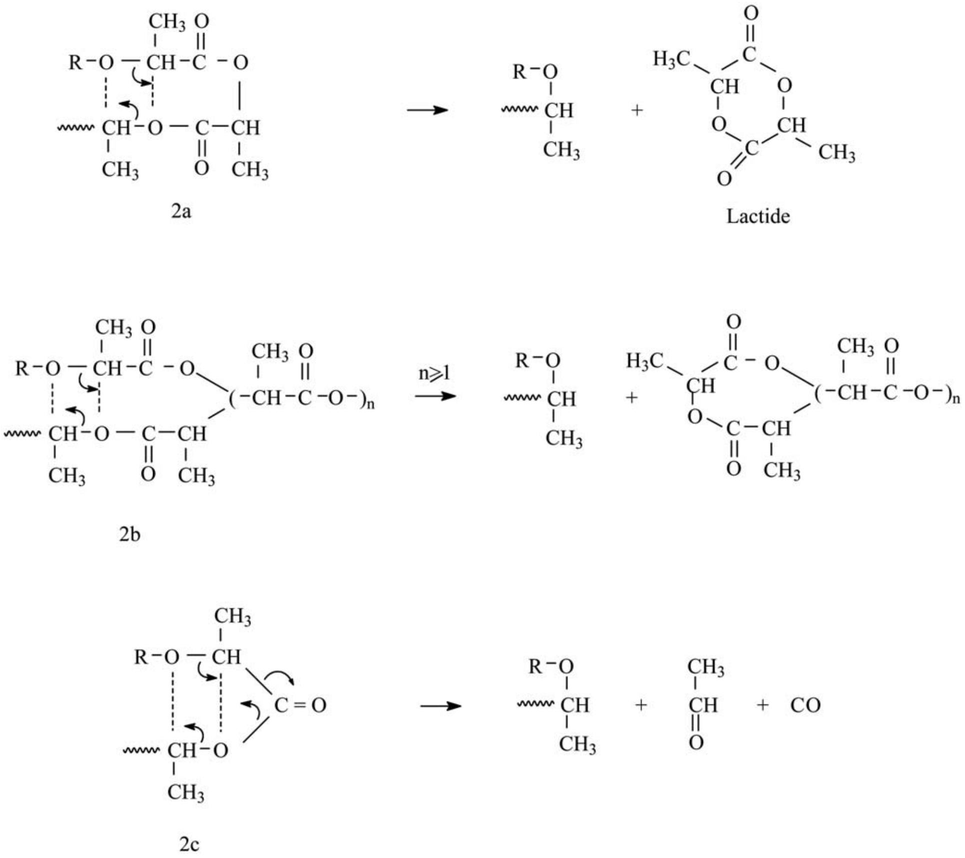
Sample	% C=O (1758/ 1455 cm^{-1})	% O—C—CO (1092/ 1455 cm^{-1})	% C—CO—O (1185/ 1455 cm^{-1})
PLA 3	↓ 45	↓ 47	↓ 43
PLA 5	↑ 58	↑ 17	↑ 8
168	↑ 68	↑ 27	↑ 17
1010	↓ 21	↓ 31	↓ 33
1076	↑ 36	↑ 22	↑ 14
B 900	↓ 5.5	↓ 19	↓ 22

↑, Increase of groups in relation to the neat PLA (more oxidation); ↓, decrease of groups in relation to the neat PLA (less oxidation – protection effect).

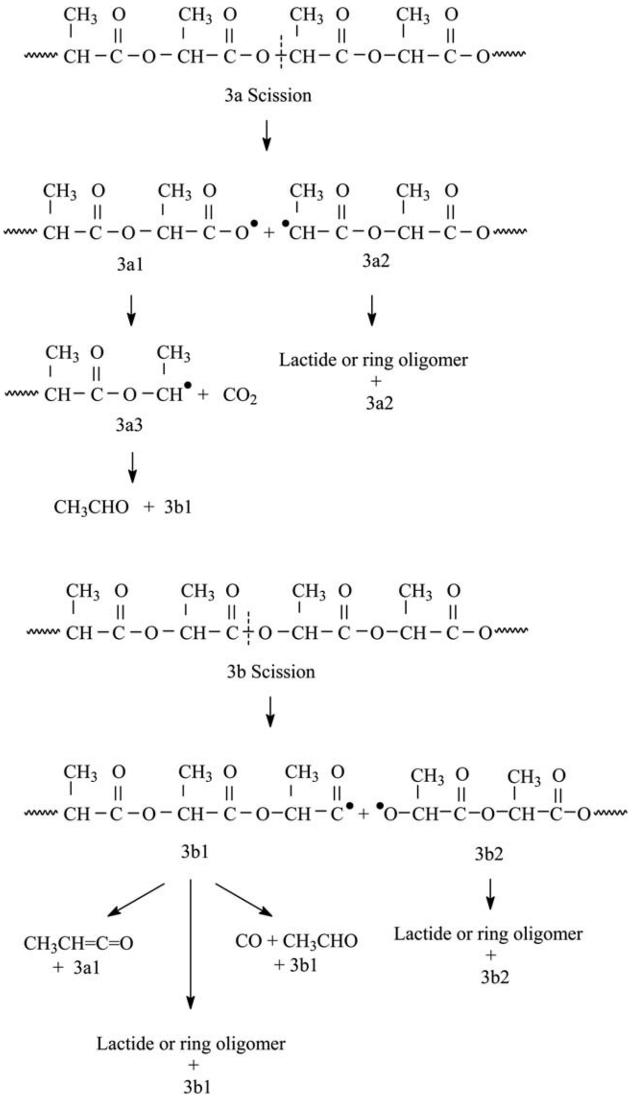
three bands of PLA, 1758, 1185, and 1092 cm^{-1}, without and with additives, processed in the temperature Profile 3 after three and five extrusion cycles. The percentage of variation was calculated in relation to the neat PLA bands (without extrusion). In this table, it was noticed that PLA submitted to three extrusion cycles decrease 45% in the carbonyl and 47% in the ester groups indicating a chain scission process. After five extrusion cycles, the ratio of the three bands increased mainly the carbonyl band (58%). It probably occurred due the chain oxidation caused by extensive thermal degradation process.

After five extrusion cycles, samples of PLA with Irgafos 168 presented the undesired result due increasing of carboxyl groups because of intense chains oxidation. The performance of the Irganox 1076 was less efficient than the Irganox 1010 and B 900. Both of stabilizers, Irganox 1010 and B 900 could prevent the molecular scissions and oxidative reactions of the PLA. The desired performance attributed to B 900 stabilizer by FTIR analysis was also verified by SEC (see results in Table VI). As mentioned before the best performance is attributed to B 900 stabilizer due this additive can act by two different mechanisms while the others only act by one mechanism.

Kopinke et al.[20] have cited McNeill and Leiper[21] to explain the thermodegradation mechanism of PLA. The authors considered several molecular and radical reactions. According to McNeil and Leiper the main reaction is a nonradical with intramolecular trans-esterification from the end of the chain (backbiting) or in the middle of the chain. Depending of the point in the backbone at which this reaction occurs, the final product could be a lactide molecule (Scheme 2a), an oligomeric ring with more than two repeat units (Scheme 2b) or acetaldehyde plus carbon monoxide (Scheme 2c). As it can be seen in Scheme 2, all these reactions lead to a reduction of molecular weight. The authors said that radical reactions only occur at temperature above 270°C. These results are from PLA samples degraded in sealed



Scheme 2. Nonradical reactions of the PLA decomposition.[20]



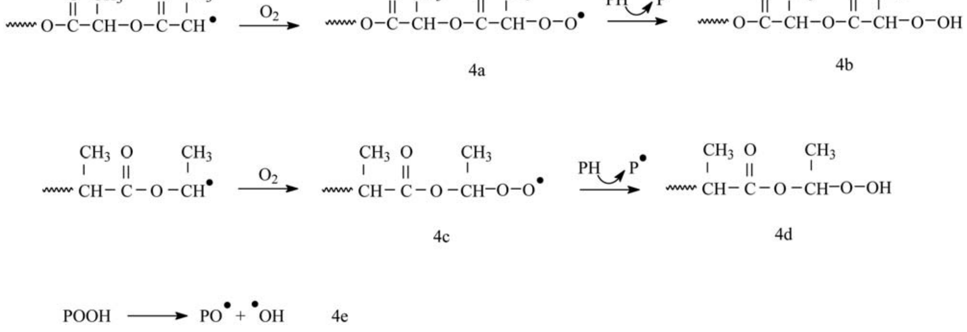
Scheme 3. Radical reactions of the PLA decomposition alkyl (a) and acyl-oxygen (b) homolysis.[20]

glass tubes and inserted into the oven under inert atmosphere without being subjected to any shear.[21] Even though the temperature used here was less than 270°C, the radical reactions have to be considered due to the high level of shearing and the oxygen presence inside the extruder. The high level of shear leads to decreasing of carbon-oxygen bonding energy and alkyl and acyl-oxygen homolysis could occur on the backbone of PLA (Scheme 3). The radical reactions proposed to thermodegradation of PLA by McNeill and Leiper[21] do not take into consideration the presence of oxygen and any peroxyl radical could be seen. Scheme 4 shows the peroxyl macroradicals (4a and 4c) generated by PLA in the presence of oxygen under melting temperature. These radicals could react with macromolecule (PH) and hydroperoxides are formed (4b and 4d). The energy of the O—O bond of hydroperoxides is very low, and may cause homolytic breakage of the O—O bond, according to Scheme 4e, leading to the formation of new free radicals that can cause chain scission or crosslinking.

Stabilizers that act directly on the deactivation of free radicals are called "primary stabilizers" and those who act in the deactivation or hydroperoxide decomposition are called "secondary stabilizers." The primary antioxidant has hydrogen that can be captured by free radicals of PLA generating by thermodegradation. These free radicals are deactivated, thus generating a free radical $X^\bullet$ located on the stabilizer molecule (Scheme 5a and 5b). This radical $X^\bullet$ has little reactivity, with a strong steric hindrance or a low diffusion coefficient. Examples for this type of additives are Irganox 1010 and 1076 used in this work. Secondary stabilizer acts transforming the hydroperoxide into not radical products, less reactive and more thermally stable (Scheme 5c). Irgafos 168 is an example for the secondary antioxidant.

From the foregoing, during the extrusion process of PLA two types of degradation reactions could occur, radical and nonradical. It was expected that the presence of the additives could prevent the molecular weight decreasing of PLA when exposed to melting temperature and shearing; however, they only can avoid the scission chains from radical reactions. It explains the lower performance of the additives.

The MFI, SEC, and FTIR analysis showed that the best performances are attributed to Irganox 1010 and B 900. A good performance of stabilizers is linked to several things: concentration, polymer compatibility, and diffusivity. The last one is correlated to molecular weight of the stabilizers. Stabilizers data sheet indicates the concentration and which are the polymers that the additive could be applied (polymer compatibility). The concentrations and the type of the additives were based according to the data sheet of the stabilizer producer; even PLA is not listed



Scheme 4. Hydroperoxides formation and decomposition during the thermo-oxidation of PLA.

$$P^{\bullet} + XH \longrightarrow PH + X^{\bullet} \qquad (5a)$$

$$POO + XH \longrightarrow POOH + X^{\bullet} \qquad (5b)$$

$$POOH + YH \longrightarrow Y{=}O + POH \qquad (5c)$$

Scheme 5. Stabilization mechanism of primary (a, b) and secondary antioxidants (c).

there. However, Irganox 1010 and blends with Irgafos 168 (Irganox B 900) are the most suitable to stabilize polyesters during the processing according to them. Furthermore, Irganox 1010 has the largest molecular weight among all stabilizers (1178 g/mol) followed by Irgafos 168 and Irganox 1076 (646.9 and 531 g/mol, respectively). Probably, the Irganox 1076 and Irgafos 168 concentrations (0.4 and 0.8 w/w%, respectively) were higher than necessary and the final effect was pro-oxidant.[22] The pro-oxidant effect is also related to PLA hygroscopicity that leads to stabilizer hydrolyzes during extrusion. Hydrolyze of these additives is very well known in the literature.[23,24] The concentrations of Irgafos 168 and Irganox 1076 in the blend (0.16 and 0.04 w/w%, respectively) were enough to obtain a positive and synergetic effect of these additives.

All results presented here confirm the need to evaluate the type and concentration of stabilizers. The results also showed that the degradation mechanism has to be understood even that the right choice of stabilizer (type and concentration) could not be enough to protect the polymer.

CONCLUSIONS

In this work, the thermal degradation and stabilization of PLA were studied using subsequent extrusion cycles. Four different additives were used, Irganox 1010, Irganox 1076, Irganox B 900, and Irgafos 168. The MFI and SEC analysis show that the mainly thermodegradation mechanism is governed by scission reactions. FTIR analysis confirmed the SEC results and showed that the synergetic effect of primary and secondary antioxidant is a suitable way to thermostabilize the PLA. Molecular weight of the additives was very important to achieve thermostabilization of PLA. However, the stabilizing effect was suppressed by the presence of nonradical reactions that occurred during the exposition of PLA to higher temperatures and shear. These results show the stabilizing ability of the PLA, consequently increasing its lifetime and the biodegradability characteristic triggered only when desired.

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