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*Article*

# Cellulosic Waste Deriving Filler Content Effect on Biodegradation Behavior and Thermal Properties for HDPE and PLA Composites

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**Abstract:** Composites with HDPE and PLA matrix have been tested to analyse the effect of natural fillers (wood flour, recycled waste paper and a mix of both fillers) and temperature on polymer degradation. Composting tests have been performed in both mesophilic (35°C) and thermophilic (58°C) conditions. Degradation development has been evaluated through mass variation, TGA and DSC. HDPE, as expected, did not display any relevant variation, confirming its stability under our composting conditions. PLA is sensibly influenced by temperature and humidity, with higher reduction of Mw when composting is performed at 58°C. Natural fillers seem to influence degradation process of composites, already at 35°C. In fact, degradation of fillers at 35°C allows a mass reduction during composting of composites, while neat PLA do not display any variation.

**Keywords:** biodegradation; bio-derived polymer; composites

## 1. Introduction

Degradation is a typical phenomenon of polymer materials leading to fragmentation and significant changes in the structure of the material characterized by the loss of some properties (e.g. mechanical properties, viscosity, molecular weight...)[1-2]. Degradation can occur in different ways such as thermal degradation, photo degradation, oxidative degradation, mechanical degradation, hydrolysis reaction with water (hydrolytic degradation) and action of microorganisms such as bacteria, fungi or algae (biodegradation) [3-5].

In general, the degradation pathways associated with polymer degradation are often determined by environmental conditions, depending on aerobiosis (presence of oxygen) or anaerobiosis (absence of oxygen), and it is based on oxidation or hydrolysis reactions [6-8]. These reactions can take place simultaneously or in succession. Anaerobic biodegradation is characterized by three main phases: firstly, hydrolysis occurs, making available molecules for bacteria digestion, secondly acid and acetogenesis convert sugars and amino acids into CO2, H2, NH3 and acetic acid [9-10]. Finally, methanogenesis produces methane, CO2 and water. Macroscopically, biodegradation appears as yellowing, fragmentation and breakage [11]. Aerobic degradation, when O2 is available, is characterized by the decomposition of polymers by oxidation which can be followed by hydrolysis of the oxidation products whose final products will be microbial biomass, CO2 and H2O. Biodegradability can be evaluated through several standards, depending on the final application of the tested materials. Several studies have been performed in order to evaluate biodegradability behavior of bio-derived polymers and composites, or to verify the effect of pro-oxidant on oil-based polymers [12-14]. The purpose of this work is to evaluate the effect of natural fillers on biodegradability of bio-derived and oil-based polymers. In 1993, Sinclair et al. already [15] patented

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blends of polylactic acids with traditional oil-based polymers, aiming to produce blends with environmentally degradable features. They obtained partially degradable materials, in which PLA rapidly decomposed, compared to stable traditional polymers. The interesting aspect is the higher rapidity of degradation of these blends in comparison to conventional non-degradable plastics because of two simultaneous aspects: firstly, PLA degradation, secondly this degradation allows the formation of high specific surface area that is expected to accelerate the process. Environmental consciousness has attracted many interests during last years, directing researches through the use of bio-derived polymers and natural fillers [16-18]. In fact, composites with natural fillers gain great attention during last decades [19-21]. Lignocellulosic fibers are characterized by a chemical composition influenced by genetic and environmental factors. In general, lignocellulosic fibers are mainly composed of cellulose (linear macromolecules of glucose units, the higher the amount of cellulose the higher the hydrophilicity of the fibers), hemicellulose (composed of several polysaccharides) and lignin (irregular and insoluble polymer, composed of aromatic units characterized by highly networked structures) [21-22]. Chemical structure of lignocellulosic fibers directly affects not just mechanical properties, but also biodegradability. In fact, each constituent of lignocellulosic fibers can be more or less susceptible to enzymatic hydrolysis, depending on the particular chemical structure [23]. Generally speaking, biological degradation occurs firstly for hemicellulose, then amorphous cellulose and lately for crystalline cellulose [24]. In fact, packed structures are less accessible for microorganisms, preventing macromolecules degradation. Biodegradation occurs through breakage of β 1,4-xylan bonds of hemicellulose by xylanase, β 1,4 glycosidic bonds of cellulose by cellulase and lignin biodegradation thanks to ligninolytic fungi actions.

In our work, samples have been subjected to composting in soil for three months at 35°C and 58°C, in order to evaluate their degradation. In particular, HDPE-based and PLA-based composites have been tested to analyze the effect of natural fillers (wood flour, recycled waste paper and a mix of both fillers) on polymer degradation. Both mesophilic and thermophilic conditions have been tested to analyze also temperature influence on composting processes.

## 2. Materials and Methods

### *2.1. Materials*

Eraclene MP90, commercial name of high-density polyethylene (HDPE) from ENI (Versalis), has been selected as oil-based polymer. Among its properties are: a melt flow index (MFI) of 7 g/10 min (190°C/2.16kg), a nominal mass of 0.96 g/cm$^3$, a tensile strength of 21 MPa, a tensile modulus of 1.2 GPa, a Shore D hardness of 50. Poly(lactic acid) (PLA) Ingeo Biopolymer 3251D from Nature Works was selected as bio-derived thermoplastic polymer, with a MFI of 35 g/10min (190°C/2.16 kg). This polymer is characterized by density 1.24, crystalline melting temperature in the range 155-170 °C and a glass transition temperature in the range 55-60°C. La.So.Le/est/Srl (Udine, Italy) provided the WF (European beech) with dimensions derived from datasheet: >500 μm 0-5%, >300 μm 20-70%, >180 μm 20-80%, <180 μm 0-5%. Recycled waste paper, whose production process is deeply described in another work [20], have been observed with optical microscopy. Average length of 750±300 μm and diameter of 25±10 μm have been measured. PLA, WF and recycled waste paper were dried one night at 80°C under vacuum, before processing.

A Micro 15 Twin-screw DSM research extruder was used at 180°C, with screw speed of 75 rpm, N2 atmosphere and 4 min residence time. The injection molding temperature was 55°C, and pressure parameters were depending on the formulation specificities because of different viscosities. Disk of 40mm diameters and 1.5mm thickness have been produced.

### *2.2. Composting tests*

Tests were performed in order to analyze the effect of testing temperature, wood flour (WF) and cellulosic fibers (P) on HDPE and PLA, as well as the behavior of soy protein isolate (with 30% of glycerol as plasticizer), used as positive reference. Tests duration was three months, keeping samples

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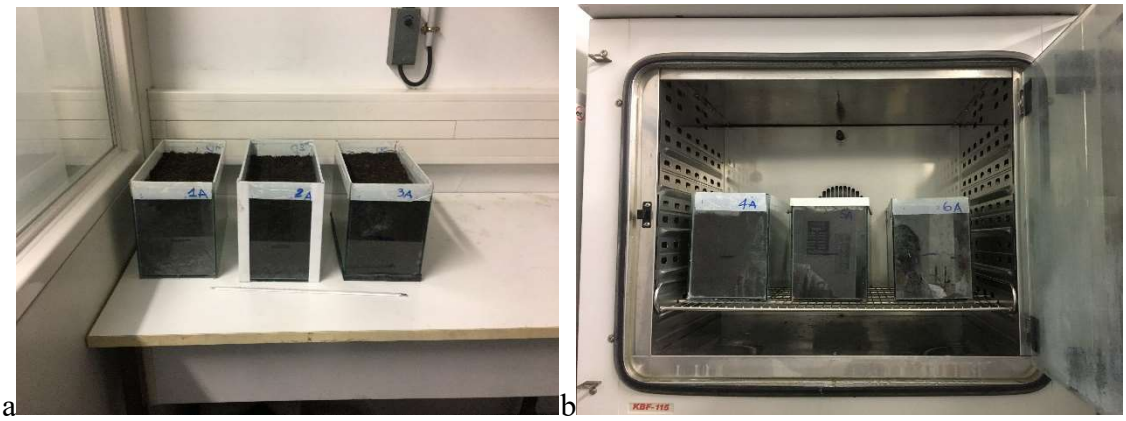
under both mesophilic (35°C) and thermophilic (58°C) conditions [25]. In each aquarium, 2kg of compost have been used: 1 kg has been put at the bottom, samples have been placed and then 1 kg of compost has been used to bury samples. During the test humidity has been checked and keept at constant value. Before burying, all samples have been dried all night under vacuum at 50°C and weighted. Table 1 displays all formulations subjected to this test. Figure 1 displays composting tests setup.

**Table 1.** Formulations of samples for composting test in soil.

| Samples | HDPE (%) | PLA (%) | Wood Flour (WF) (%) | Recycled Waste Paper (P) (%) |
|---|---|---|---|---|
| HDPE | 100 | | | |
| PLA | | 100 | | |
| HDPE60-WF40 | 60 | | 40 | |
| HDPE60-P40 | 60 | | | 40 |
| PLA60-WF40 | | 60 | 40 | |
| PLA60-P40 | | 60 | | 40 |
| PLA60-WF30-P10 | | 60 | 30 | 10 |



a b

**Figure 1.** Composting tests setup at 35°C (a) and 58°C (b).

Each month a disk per formulation is taken from the aquarium, washed with distilled water and dried until constant weight is reached. The evolution of degradation is analysed by mass variation of each samples as:

$$\Delta M(\%)=(M_{t0}-M_t)/M_{t0} *100$$

In which ΔM(%) is mass variation, Mt0 is mass value before composting and Mt is mass value at time t (respectively 1,2 3 months at 35°C and 58°C). Moreover, other tests have been performed to analyze degradation evolution, such as: Thermogravimetric analysis (TGA) carried out on a Q500 Thermal Analysis instrument, up to 600°C with a scanning temperature of 10°C·min-1 under a nitrogen flow of 50mL·min-1 and Differential scanning calorimetry (DSC) performed on a Q20 Thermal Analysis instrument with two cycles (with a 4 minutes interval between them) at 180°C to eliminate trace of thermal history. The first cycle is carried out from 25°C to 180°C at 10°C·min-1 under a nitrogen flow of 50 mL·min-1 followed by a cooling from 180°C to 25°C at 10°C·min-1 Tc and ΔHc were measured during this cooling phase. Then, a second heating from 25°C to 180°C at 10°C·min-1 enables to

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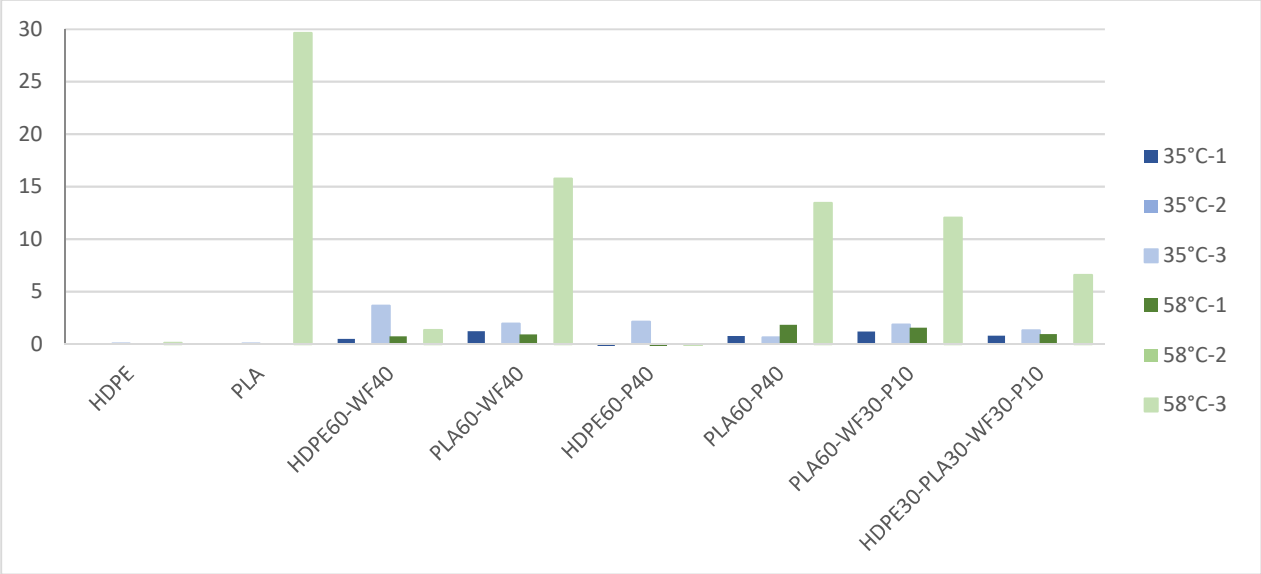
119 determine. Tcc, Tf and ΔHf. Infrared Analysis Attenuated Total Reflection (ATR-FTIR) tests were
120 carried out with a thermo-scientific Nicolet IS10 spectrometer, with a spectral range 4000-400 cm-1
121 and 32 scans.

122 **3. Results**

123 As expected, HDPE displays no mass variation at both 35°C and 58°C, in agreement with
124 literature [26], as visible from Figure 2Figure 1. The addition of wood flour and recycled waste paper
125 influenced mass variation. Probably mass variation is related to natural fillers degradation, especially
126 for wood flour addition [27]. PLA-based samples, thanks to PLA biodegradability, display mass
127 variation, especially after three months at 58°C.




128

129 ***Figure 2.*** Mass variation measurements of HDPE, PLA, HDPE60-WF40, PLA60-WF40, HDPE60-P40,
130 PLA60-P40 and PLA60-WF30-P10 for three months testing in soil at 35°C and 58°C.

131 In agreement with literature results [28], PLA is normally characterized by a first lag phase, in
132 which diffusion of water occurs and macromolecules are still too long to be degraded by
133 microorganisms. As a consequence, mass variation displays a higher difference for time 3 with
134 respect to time 1 and 2. A visible effect of temperature is displayed for neat PLA degradation process.
135 In fact, samples at 58°C are characterized by a higher degradation rate and higher mass variation
136 with respect to samples at 35°C. PLA degradation is due to breakage of ester bonds. Water
137 hydrolyses polymer chains randomly., As a consequence, polymer molecular weight is reduced, and
138 oligomers are obtained. In fact, degradation can be evaluated through mass variation [29]. Wood
139 flour and recycled waste paper addition seems to increase mass variation for PLA-based samples at
140 35°C. This can be related to humidity absorbed by wood flour and recycled waste paper [30].
141 Moreover, a degradation of natural fillers can also occur, reducing sample's mass. PLA-based
142 composites at 58°C are characterized by a lower mass variation with respect to neat PLA. This effect
143 could be related to increased crystallinity of PLA due to fillers addition [31]. Visual observation of
144 samples is visible in figure 3, and agrees with mass variation results.

145 **Table 2.** SEC results for PLA-based samples after composting tests at 35°C and 58°C.

| | $\overline{M_w}$ (Da) | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | 35°C | | 58°C | | |
| | t0 | t1 | t2 | t3 | t1 | t2 | t3 |
| PLA | 41832 | 41782 | 45782 | 44912 | 35324 | 8606 | 5083 |
| PLA60-WF40 | 41925 | 41725 | 39316 | 39202 | 30179 | 18692 | 5334 |

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| | | | | | | | |
|---|---|---|---|---|---|---|---|
| PLA60-P40 | 43283 | 43052 | 43576 | 42529 | 34934 | 19898 | 5771 |
| PLA60-WF30-P10 | 42274 | 42069 | 39060 | 38409 | 32402 | 23374 | 5222 |

Mass-average molecular weight ($\overline{M_w}$) in mesophilic conditions (35°C) did not display sensitive variations, suggesting a slow PLA degradation. In fact, the first step of PLA degradation is characterized by hydrolysis. This process allows chain scissions until $\overline{M_w}$ reach suitable chain length for microorganisms attack [32]. Mesophilic condition seems to be insufficient to reduce PLA $\overline{M_w}$ because of limited water diffusion and action on ester groups [33]. PLA-based composites, both with wood flour and recycled waste paper, still display small Mw variations. PLA-based samples tested in thermophilic conditions (58°C), conversely, displayed $\overline{M_w}$ sensitive reduction by time: in fact, $\overline{M_w}$ decreased from about 40kDa to about 5kDa after three months. PLA degradation hydrolytic step, in agreement with literature results [34], is temperature sensitive, displaying optimal kinetic condition around 58°C. However, recycled waste paper seems to partially hinder PLA degradation with respect to wood flour, keeping $\overline{M_w}$ at slightly higher values. In any case, the addition of cellulosic fillers seems to increase PLA crystallinity, affecting water diffusion. As a consequence, a lower degradation phenomenon is displayed by composites with respect to neat PLA [35-36].

Thermogravimetric analysis has been performed on pure HDPE and on HDPE composites filled with wood flour and recycled paper, at time 0 and after 30, 60 and 90 days of composting at temperatures of 35°C and 58 °C. Observing thermograms, the presence of fillers reduces thermal stability of samples by lowering the onset temperature degradation compared to neat HDPE. Low degradation temperatures of paper and wood flour are due to the presence of hemicellulose, cellulose and lignin that are sensitive to thermal degradation [32-34, 37].

HDPE, for all time (table 3), as reported in literature [32-34, 37], is thermally stable up to temperatures of about 450 ° C and then quickly starts to degrade, with a maximum weight variation speed around 480 ° C. Samples do not display significant variations in both onset temperature and temperature of the maximum weight variation for HDPE. The degradation leads, in all cases, to a total loss of mass because of thermal cracking ending around about 500 ° C [32-34, 37]. HDPE60-WF40 and HDPE60-P40 display a multistep thermal degradation (**Error! Reference source not found.** and 5). Firstly, moisture evaporation from room temperature to about 100°C. Secondly, thermal degradation of hemicellulose, the most thermal sensitive component in lignocellulosic fillers [38], occurs around 295°C. Cellulose pyrolysis is displayed at higher temperature range (315-400 ° C) [37-40], and around 350 ° C the maximum thermal degradation rate of cellulose and lignin is displayed. For temperatures higher than 400°C, almost all cellulose is pyrolyzed, while lignin decomposes more slowly, over 400 °C and with a higher amount of solid residue. Samples display, considering composting progression up to time 3, a modest reduction in the initial degradation temperature with a reduction in the residual mass. HDPE60-P40, rich in cellulose, displays a residual mass approximately unchanged at around 5%, while HDPE60-WF40, due to the higher lignin content, displays higher residual mass [39]. Moreover, HDPE60-WF40 displays reduction of residual mass of samples after composting process from 11% to 7%.

**Table 3.** TGA results for HDPE and PLA based composites after three months buried at 35°C and 58°C.

a) Tonset results, b) Tpeak results, c) Δm results.

a

| | | | 35°C | | | 58°C | |
|---|---|---|---|---|---|---|---|
| | | | Tonset (°C) | | | Tonset (°C) | |
| | t0 | t1 | t2 | t3 | t1 | t2 | t3 |
| HDPE | 451 | 461 | 464 | 464 | 459 | 471 | 468 |
| HDPE60WF40 | 295 | 295 | 297 | 297 | 300 | 291 | 283 |
| HDPE60P40 | 313 | 14 | 304 | 308 | 305 | 294 | 298 |

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| | | | | | | | |
|---|---|---|---|---|---|---|---|
| PLA | 318 | 333 | 296 | 324 | 302 | 258 | 240 |
| PLA60WF40 | 296 | 295 | 293 | 291 | 296 | 280 | 248 |
| PLA60P40 | 323 | 318 | 309 | 315 | 297 | 297 | 242 |
| PLA60WF30P10 | 301 | 307 | 299 | 297 | 298 | 297 | 254 |

b

| | | | 35°C Tpeak (°C) | | 58°C Tpeak (°C) | | |
|---|---|---|---|---|---|---|---|
| | **t0** | **t1** | **t2** | **t3** | **t1** | **t2** | **t3** |
| HDPE | 477 | 481 | 481 | 481 | 479 | 484 | 484 |
| HDPE60WF40 | 356/483 | 350/483 | 340/483 | 336/480 | 341/482 | 351/485 | 333/484 |
| HDPE60P40 | 344/484 | 346/483 | 336/483 | 346/484 | 333/484 | 326/477 | 320/298 |
| PLA | 343 | 356 | 320 | 351 | 336 | 298 | 271 |
| PLA60WF40 | 321 | 314 | 313 | 313 | 316 | 306 | 269 |
| PLA60P40 | 344 | 337 | 330 | 333 | 316 | 324 | 264 |
| PLA60WF30P10 | 327 | 327 | 321 | 316 | 321 | 307 | 275 |

| | | | 35°C Δm (%) | | 58°C Δm (%) | | |
|---|---|---|---|---|---|---|---|
| | **t0** | **t1** | **t2** | **t3** | **t1** | **t2** | **t3** |
| HDPE | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| HDPE60WF40 | 91 | 89 | 90 | 93 | 91 | 91 | 91 |
| HDPE60P40 | 95 | 94 | 95 | 95 | 93 | 94 | 93 |
| PLA | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| PLA60WF40 | 89 | 88 | 88 | 91 | 90 | 91 | 96 |
| PLA60P40 | 94 | 94 | 94 | 95 | 89 | 93 | 93 |
| PLA60WF30P10 | 90 | 89 | 92 | 93 | 91 | 91 | 91 |

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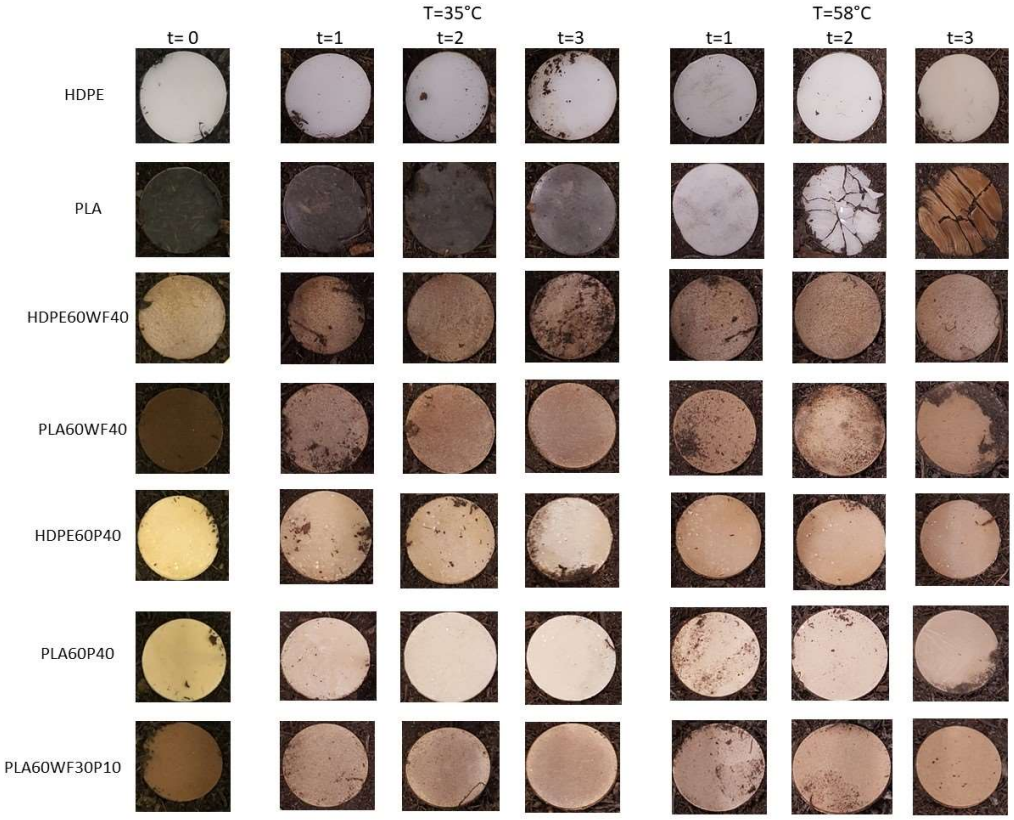


***Figure 3.*** Visual observation of samples at time 0, and after 1,2 and 3 months buried at 35°C and 58°C.

PLA-based samples have also been analyzed by SEC in tetrahydrofuran, in order to evaluate average molecular weight variation during composting at 35°C and 58°C (Table 2).

**Table 2.** SEC results for PLA-based samples after composting tests at 35°C and 58°C.

| | $\overline{M_w}$ (Da) | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | 35°C | | | 58°C | |
| | t0 | t1 | t2 | t3 | t1 | t2 | t3 |
| PLA | 41832 | 41782 | 45782 | 44912 | 35324 | 8606 | 5083 |
| PLA60-WF40 | 41925 | 41725 | 39316 | 39202 | 30179 | 18692 | 5334 |
| PLA60-P40 | 43283 | 43052 | 43576 | 42529 | 34934 | 19898 | 5771 |
| PLA60-WF30-P10 | 42274 | 42069 | 39060 | 38409 | 32402 | 23374 | 5222 |

TGA curves of PLA display, over time, a significant difference in thermal stability between samples at 35 ° C compared to 58 ° C. Mesophilic conditions display a reduction of thermal stability only at time 3. Graphs display a single peak of maximum decomposition rate which starts at about 320 ° C and at 350 °C. PLA is completely degraded with no residual mass. Samples after burying at 58 ° C, on the other hand, display a thermal stability reduction over time, possibly related to the presence of shorter macromolecules compared to time 0, because of degradation process [41]. The onset temperature at time 3 is about 240 ° C and, at 300 ° C, PLA is completely degraded with no residual mass.

The addition of wood flour, for samples buried at 35°C, reduces thermal stability of the composite compared to neat PLA. Samples buried at 58°C, on the other hand, display a progressive

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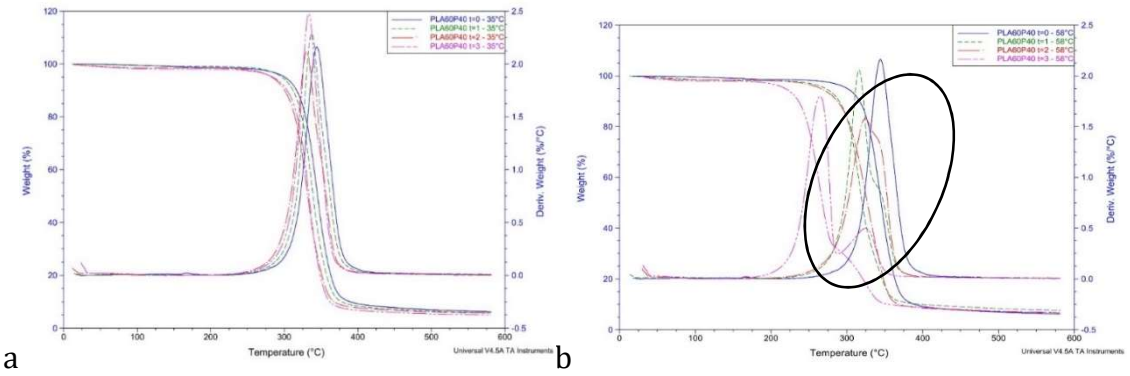
reduction of stability over time, but higher than neat PLA. This trend is due to the hemicellulose and PLA degradation during composting process. Thermograms display that thermal decomposition of PLA60-WF40 composite occurs between 150 and 450°C. In mesophilic and even more evident in thermophilic conditions, the presence of "shoulders" due to the overlapping of cellulose and lignin bands is highlighted. PLA, under composting conditions, displays a reduction in onset temperature degradation and sample is progressively more enriched in cellulose. As a consequence, after composting process, two separate peaks are visible, the first refers to PLA and the second to cellulose [42]. A residual mass is displayed at the end of thermal degradation, decreasing over time.

PLA60-P40 displays a reduction in thermal stability with respect to neat PLA. Thermograms display a single peak for samples buried at 35°C, with a slight decrease in thermal stability over time. Samples at 58°C display higher reduction of thermal stability and the appearance of shoulder, already displayed for PLA60-WF40, becomes more visible over time (**Error! Reference source not found.**). All samples display a reduction of onset temperature with respect to PLA60-WF40, possibly associated with the lower presence of hemicellulose in paper. A residual mass is displayed at the end of thermal degradation, in lower amount than PLA60-WF40, which remains stable over time due to the lower presence of lignin and hemicellulose [43].




a b

**Figure 4.** Mass and derivative variations in weight as a function of temperature during the degradation of PLA60-P40 at month 0, 1, 2, 3 at 35 ° C (a) and 58°C (b).

DSC analyses allow understanding the influence of natural fillers on both HDPE and PLA thermal properties, but also the influence of composting process on materials. Neat HDPE display, as expected, no sensitive variation of melting temperature after composting at both 35°C and 58°C. HDPE-based composites with WF and P display higher melting and crystallization enthalpies values compared to neat HDPE. Similar observations are in agreement with results of Lee et al., who have studied the influence of different types of softwood in HDPE matrix composites [44]. This effect is more evident for P than for WF, probably because of morphological differences between P (fibrous) and WF (particulate). No sensitive variations are displayed with DSC analyses for HDPE-based samples, probably because degradation mainly occurs on natural fillers, keeping unchanged HDPE. No sensitive variations have been displayed for PLA after composting at 35°C and the curves are almost superimposable, in agreement with no mass and Mw variation. Samples after composting at 58°C (**Error! Reference source not found.**), instead, as the composting process proceeds, show a decrease in glass transition temperature (Tg), from 61°C to about 40°C after three months. Moreover, typical cold crystallization temperature (Tcc) displays a decrease at 58°C during the degradation process. This reduction may be associated with the formation of oligomers of lactic acid resulting from the cleavage of chains due to hydrolysis during composting, as confirmed also by Mw reduction. Chains with lower molecular mass crystallize more easily and have lower cold crystallization temperatures [45]. No crystallization during cooling has been detected during DSC analyses for neat PLA.

**Table 4.** DSC results for neat PLA during composting process at 58°C.

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| | Tm (°C) | ΔHm PLA ($J/g_{PLA}$) | Tcc (°C) | Tg (°C) |
|---|---|---|---|---|
| PLA t0 | 169 | 48 | 100 | 61 |
| PLA t1 | 166 | 53 | 94 | 55 |
| PLA t2 | 148 | 47 | 84 | 45 |
| PLA t3 | 144 | 45 | 90 | 41 |

The presence of wood flour and recycled waste paper in PLA60-WF40, PLA60-P40 and PLA60-WF30-P10 seems to obstacle cold crystallization, not detected for these samples, because of nucleating effect of natural fillers, facilitating crystallinity from molten state. As a consequence, a formation of two melting peaks was evident (as visible from **Error! Reference source not found.**), indicating the presence of two crystalline fractions. Moreover, thermograms of samples buried at 35 ° C are almost superimposable for all composites, while at 58°C there is a displacement of melting peaks towards lower temperatures. $\overline{M_w}$ reduction, due to degradation progression, is responsible for Tg, Tcc and Tm reduction. In fact, the lower chain length, the easier the chain mobility [46]. In fact, under mesophilic conditions, melting temperature Tm does not show significant variations compared to neat PLA. Samples buried under thermophilic condition display a significant reduction of Tm over time (**Error! Reference source not found.**). This reduction is analogous to the one displayed by neat PLA, and is probably associated with a decrease in Mw, although Tm of PLA-based composites are still higher than Tm of PLA.

**Table 5.** DSC results for PLA-based composites during composting process at 58°C.

| | Tm (°C) | ΔHm PLA (J/gPLA) |
|---|---|---|
| PLA60-WF40 t0 | 169 | 54 |
| PLA60-WF40 t1 | 166 | 53 |
| PLA60-WF40 t2 | 156 | 69 |
| PLA60-WF40 t3 | 148 | 45 |
| | | |
| PLA60-P40 t0 | 171 | 53 |
| PLA60-P40 t1 | 168 | 59 |
| PLA60-P40 t2 | 162 | 62 |
| PLA60-P40 t3 | 153 | 56 |
| | | |
| PLA60-WF30-P10 t0 | 168 | 55 |
| PLA60-WF30-P10 t1 | 167 | 62 |
| PLA60-WF30-P10 t2 | 160 | 69 |
| PLA60-WF30-P10 t3 | 151 | 47 |

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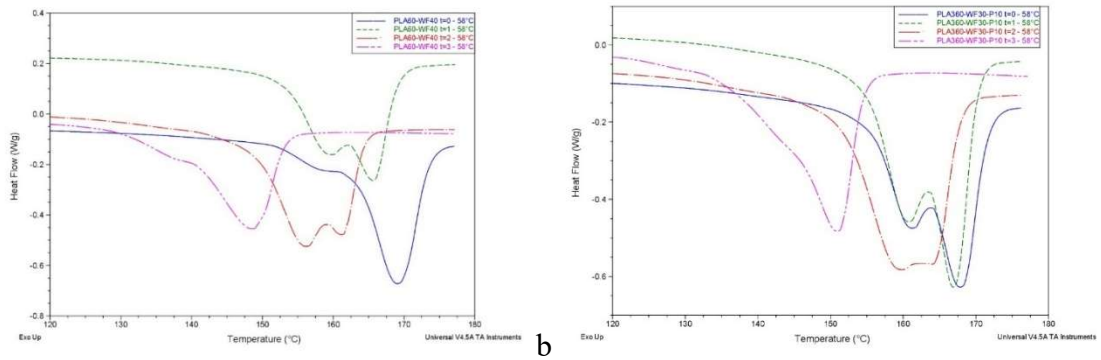


**Figure 5.** Melting peak of PLA60-WF40 (a) and PLA60-WF30-P10 (b) composites during composting process at 58°C.

FTIR analyses validate the others obtained results. HDPE did not display any modification of its spectra after three months buried in soil at both 35°C and 58°C. Spectra of HDPE60-P40 combine the absorption bands of HDPE matrix and characteristic absorption peaks of cellulose. Paper consists mainly of cellulose fibres but also contains hemicellulose and lignin [47]. Cellulose is characterized by a) peak at 1425 cm-1, known as the crystalline band, caused by the vibrations of the aromatic skeleton combined with the bending of the C-H (a lowering of its intensity reflects the decrease in the degree of crystallinity of samples), b)peak at 1032 cm-1, associated both with the symmetrical CO stretching of the cellulose and with the CO deformation of the primary alcohols in the lignin, c) peaks between 3400-3300 cm-1 and 1593 cm-1 attributed to the stretching and bending, respectively, of OH groups of cellulose [47-49]. This modification, together with the shift of peak at 1316 cm-1 towards higher values, denotes the development of new inter- and intramolecular hydrogen bonds. The predominant degradation phenomenon that characterizes the filler is oxidative [50], especially for hemicellulose and lignin. The oxidative process is detected by increasing intensity of the small peaks generated by the functional carbonyl group in the absorption range between 1800-1600 cm-1. In particular, small signals revealed in the area 1740-1709 cm-1 are an expression of the carbonyl groups related to C = O stretching of hemicellulose groups or to the ester bond of the carboxylic group in the ferulic and coumarinic acids of the lignin and hemicellulose. This also makes this zone a good "marker" of oxidative processes, the intensity of the band around 1735 cm-1 is usually proportional to the oxidation of hemicellulose (C = O in xylan). The areas of interest for PLA at about 1750 and 1180 $cm^{-1}$ are clearly visible, which belong to the stretching C-O and to the stretching C-O-C of PLA. 1080 $cm^{-1}$ is associated to the C-C stretching. The biodegradation of polylactic acid should determine an increase of carboxylic and alcoholic groups. Over time, at 35 ° C, there are no evident peaks variation, while at 58 ° C, as the biodegradation process proceeds, PLA displays a variation related to the peak at 1750 $cm^{-1}$ due to the stretching of the C = O group. PLA biodegradation is highly sensitive to moisture, obtaining a degradation process characterized by water absorption, ester cleavage forming oligomers, solubilization of oligomer fractions and diffusion of bacteria into soluble oligomers [51]. Biodegradation of PLA should lead to an increase in carboxylic and alcoholic groups. In fact, a shift of the peak at 1750 $cm^{s}$, assigned to the stretching of the carbonyl, confirms a successful degradation. WF probably accelerated the degradation of composite during composting at 35°C, over time enriched in WF. The explanation would be attributed to a greater degradation by hydrolysis of PLA due to the presence of moisture in the wood [52]. Degradation of PLA, also for PLA60-P40, can be associated with the increase of the terminal hydroxyl peak and the variation, although not always linear (probably due to the lack of homogeneity of the sample), of the peak in the area between 1730 and 1750 $cm^{-1}$, characteristic of carbonyl groups related to C = O stretching. An increase in terminal hydroxyl peak is in agreement with a reduction in molecular mass. In conclusion, as expected, pure HDPE was non-biodegradable, while HDPE60-WF40 and HDPE60-P40 display only degradation of cellulose, lignin and hemicellulose. Neat PLA sample at 35 ° C was not very sensitive

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to degradation processes, but biodegradation was accelerated by the presence of paper and/or wood flour. At 58°C, pure PLA is easily biodegradable, and signs of biodegradation increase over time. PLA-based composites are characterized by PLA degradation and enrichment in cellulose, less sensitive to biodegradation.

## 4. Conclusions

HDPE-based and PLA-based composites have been tested to analyze the effect of natural fillers (wood flour, recycled waste paper and a mix of both fillers) on polymer degradation. Moreover, samples made of HDPE-PLA blend and a mix of two fillers have also been tested. Future studies have to be done in order to complete the study on the effect of these fillers on HDPE and PLA composting features. In fact, PLA is sensitive to temperature and humidity conditions, displaying higher reduction of Mw when composting is performed at 58°C. Moreover, natural fillers seem to influence mass variation, already at 35°C. In fact, degradation of fillers at 35°C allows a mass reduction during composting of composites, while neat PLA do not display any variation. These results are in agreement with other analyses performed (TGA, DSC), validating natural filler degradation under composting conditions.

**Conflicts of Interest:** The authors declare no conflict of interest.

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