

## Polylactic acid and its blends with petroleum-based resins: Effects of reprocessing and recycling on properties

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**ABSTRACT:** Environmental and economic reasons make the use of bioplastics and biocomposites increasingly coveted in sectors other than packaging. Recycling of all wasted or rejected durable plastics is highly desired and biobased plastics are no exception. Therefore, the investigation of pre- and post-consumer recycling of products made from biobased plastics is of great interest. Polylactic acid (PLA) and its blends have been chosen for this study because it is an excellent representative of mass-produced bioplastics for industrial applications. As part of the “Sustainable Recycling of ‘Green’ Plastics” project, the current study addresses the durability issues related to the reprocessing and post-consumer recycling of a PLA virgin resin and two commercially available blends of PLA namely one with polycarbonate (PC) and one with polyethylene (PE). The materials were investigated using methods that simulate post-processing and post-consumer recycling. Accelerated ageing was performed at elevated temperature and humidity to simulate the usage period of the materials. The materials were analyzed using differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and their mechanical strength was evaluated by tensile and impact testing. The flow properties of the materials were characterized by the melt flow index (MFI). Multiple processing of pure PLA did not affect the impact strength or the glass transition temperature ( $T_g$ ), but caused crystallization and increase in the MFI, indicating that degradation occurred during processing. DSC thermograms of the blends revealed that the components in the blends were not miscible. Multiple processing of the blends did not significantly affect the elastic modulus of the materials, but affected the elongation at break. The results indicated that multiple processing of the PLA/HDPE blend caused increased dispersion and thus increased elongation at break, while the dominating mechanism in the PLA/PC blend was degradation that caused a decrease in elongation at break. Post-consumer recycling of the PLA/PC blend was simulated and the results clearly showed that ageing corresponding to one year of use caused a significant degradation of PLA. Pure PLA was severely degraded after only one ageing cycle. Although the PLA/PC blend showed some improved mechanical properties and resistance to degradation compared with pure PLA, one ageing cycle still caused a severe degradation of the PLA and even the PC was degraded as indicated by the formation of small amounts of bisphenol A. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2016, 133, 43916.

**KEYWORDS:** biopolymers and renewable polymers; blends; degradation; properties and characterization; recycling

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### INTRODUCTION

With society and industry becoming more environmentally conscious, bioplastics and biocomposites are an increasingly attractive choice for industrial applications. In particular, durable biobased plastics are forecast to increase their market share from 10% in 2010 to about 50% by 2018<sup>1</sup> because of new legislation and policies. However, the use of biobased plastics in long-term applications requires durability under much harsher conditions and longer periods compared with single-use articles. In addition, because of environmental concerns and economic reasons, the recycling of wasted or rejected plastics is highly desired.<sup>2</sup> Industrial processes have varying efficiencies, which imply that the waste fraction from production can range from a

few per cent to 80% or more. Thus, it is important for industry to be able to reprocess production waste provided that the material has retained its properties and durability. Sustainable use of biobased plastics also includes the condition for resource efficiency, which implies that materials should also be recyclable as post-consumer waste.

Polylactic acid (PLA) and its blends have been chosen for this study because PLA is an excellent representative of mass-produced bioplastics for industrial applications. It is a thermoplastic that belongs to the family of aliphatic polyesters and is made from renewable resources. It is a high-strength, high-modulus polymer that has mostly been used in packaging and biocompatible medical applications. The stereo-chemical

structure of PLA can be easily modified by polymerizing a specific mixture of the L- and D-isomers to produce amorphous or crystalline polymers of high molecular weight.<sup>3</sup> PLA homopolymers have a glass transition temperature ( $T_g$ ) of  $\approx 55^\circ\text{C}$  and a melt temperature ( $T_m$ ) of  $\approx 175^\circ\text{C}$ . The temperature required for melt processing is at least  $185\text{--}190^\circ\text{C}$ . However, at these temperatures, PLA can undergo numerous degradation reactions such as thermal unzipping degradation, oxidative chain scission, inter- or intramolecular transesterification and hydrolysis in the presence of moisture.<sup>4</sup> In addition, the degradation temperature and rate depend on low-molecular weight impurities and on the concentration of catalyst residues.<sup>5</sup>

Because of these shortcomings, many PLA suppliers have developed various grades of PLA, blended with fossil-based resins such as polycarbonate (PC) and polyethylene (PE). The benefits of these PLA blends are according to the manufacturers, improved mechanical properties, durability and lower price; moreover, the materials still possess a significant share of bio-based carbon. Despite these benefits, blends of different polymers are generally not miscible (a two-phase system) because of unfavorable entropy and enthalpy factors. In such two-phase blends, the morphology and thus the physical properties are controlled by the weight ratio of the two components, the viscosity ratio, as well as the interfacial tension between the phases.<sup>6</sup> Poor interfacial compatibility of the polymer components leads to separation between the phases at low applied stress, followed by crack formation and embrittlement. To reduce the compatibility problems, suitable compatibilizers, such as glycidyl methacrylate-grafted PE<sup>7</sup> in PLA/PE blends, and poly(butylene succinate-co-lactate) and epoxy<sup>8</sup> in PLA/PC blends have been used with some success. However, the end-of-life options for PLA and its blends have not yet been scrutinized and recycling efforts are still in their infancy because of the lack of or small volume of post-consumer waste. The current study addresses the durability issues related to the reprocessing and post-consumer recycling of PLA and two commercially available blends of PLA with HDPE and PC, respectively.

## EXPERIMENTAL

### Materials

The materials used in this study were commercially available and included one virgin PLA resin Ingeo 3051D (NatureWorks LLC, Minnetonka, MN) of injection molding grade and two blends. One blend was composed of PLA and high-density polyethylene (HDPE), with 39% PLA and was designated PLA/HDPE (39%) renewable-RTP2099X115382C. The second blend was composed of PLA and polycarbonate (PC) with 32% PLA and was designated PLA/PC (32%) renewable-RTP2099X126213. The two blends were supplied by RTP Company (Winona, MN).

### Processing

The materials were processed in a modular twin screw extruder (Plasti-Corder<sup>®</sup> Labstation + TSE 20/40D, Brabender<sup>®</sup> GmbH & Co. KG, Duisburg, Germany) with subsequent granulation of the extruded string. The applied processing parameters varied between the different materials where the melt temperature during processing was approximately  $195^\circ\text{C}$  for both the pure PLA and the PLA/HDPE blend and about  $240^\circ\text{C}$  for the PLA/PC

blend. All materials were either kept dry or dried in a vacuum oven before each extrusion, as specified in the technical data sheets, to avoid extensive hydrolysis of the polymers during processing. After each processing cycle, a small volume of each material was removed for subsequent characterization of material properties.

### Sample Preparation

The processed materials were melt-pressed into 1-mm-thick plates using compression molding equipment (Fontijne LabEcon 300). The melt-pressing temperature was set at  $205^\circ\text{C}$  for the pure PLA and the PLA/HDPE blend and  $250^\circ\text{C}$  for the PLA/PC blend. A pressure of 150 kN was applied for 2 min before the start of controlled cooling of the material using a cooling rate of  $10^\circ\text{C}/\text{min}$  (PLA) or  $15^\circ\text{C}/\text{min}$  (PLA/HDPE and PLA/PC). All samples were dried in a vacuum oven, according to specifications, before being subjected to melt-pressing.

The produced test plates were then used for the preparation of test specimens for material characterization by water-jet cutting (PLA/PC), milling (PLA), or punching (PLA/HDPE).

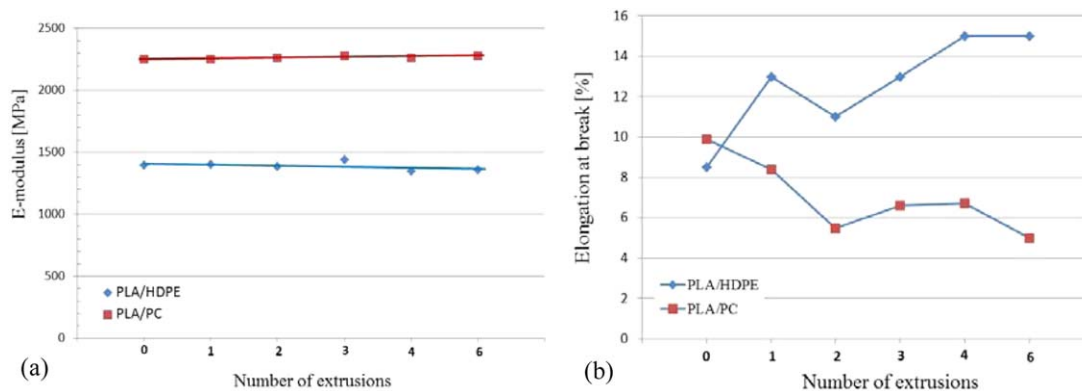
### Accelerated Ageing

Accelerated ageing was performed at elevated temperature and humidity in a Weiss WK600 climate test chamber (Weiss Umwelttechnik GmbH, Reiskirchen-Lindenstruth, Germany) to simulate the usage period of the materials. The selected ageing temperature was set at  $50^\circ\text{C}$  to be below the  $T_g$  of the PLA ( $\approx 60^\circ\text{C}$ ); the relative humidity (RH) was set at 90%. Each ageing cycle was 7 weeks, which was estimated to correspond to roughly 1 year of service at room temperature using a procedure known as the Simplified Protocol for Accelerated Aging (also called the “10-degree rule”) which was developed around the collision theory-based Arrhenius model. Many engineers and scientists are using this so called “rule of thumb” in selection of time and temperature for accelerated ageing tests. The rule tells that if the temperature is increased by 10 K, the rate of degradation reactions is doubled (the time is halved).<sup>9</sup>

### Test Methods

**Differential Scanning Calorimetry (DSC).** The DSC analyses were performed using the instruments DSC 823e and DSC 1 (heat-flux DSCs, Mettler, Toledo, OH) equipped with gas controllers and sample robots. The temperature and heat-flow accuracy of the DSCs were frequently checked using pure indium and zinc as reference materials. Small pieces of sample (5–10 mg) were subjected to temperature programs based on ISO 11357-2 and 11357-3 to record transition parameters, such as  $T_g$ ,  $T_m$ , the cold crystallization temperature ( $T_{cc}$ ), and their magnitudes. The program included rapid heating to  $180^\circ\text{C}$  to erase the thermal history of the materials, followed by slow cooling ( $-5^\circ\text{C}/\text{min}$ ) to  $20^\circ\text{C}$  and finally a second heating ( $10^\circ\text{C}/\text{min}$ ) to  $180^\circ\text{C}$ .

**Fourier Transform Infrared Spectroscopy (FTIR).** The materials were analyzed using a Nicolet iS50 FT-IR spectrometer equipped with Built-in Diamond ATR Module or a Nicolet 6700 FT-IR instrument (Thermo Electron Corporation) equipped with a micro-ATR. The analyses were performed by collecting at least two spectra (32–64 scans) from each sample.



**Figure 1.** (a) E-modulus, and (b) elongation at break versus number of extrusions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### High-Resolution Scanning Electron Microscopy (HR-SEM).

The test materials were immersed in liquid nitrogen and cryogenically fractured. The cross section was sputter coated with 10–15 nm Au/Pd. For the imaging, an instrument ZEISS SUPRA 40VP Field Emission Scanning Electron Microscope (FE-SEM) was used. The actual imaging was done in high vacuum mode with a high-efficiency In-lens detector.

**Tensile Testing.** The elongation at break and the E-modulus for each generation of the extruded and/or pressed material were measured by performing the tensile tests under standard conditions ( $23 \pm 2^\circ\text{C}$ ,  $50 \pm 10\%$  RH), using a Zwick Z100 (Zwick GmbH, Ulm, Germany) tensile tester equipped with a video extensometer. The cross-head speed was initially set at 0.5 mm/min (for E-modulus evaluation) up to an elongation of 0.5%, and then 50 mm/min until the specimen broke. Each material was evaluated by testing 5–10 dumbbell-shaped specimens with a 20 mm specimen gauge length, based on the ISO 527-2.

**Instrumented Impact Testing.** The samples were tested using an instrumented pendulum impact tester (ResilImpactor, CEAST) equipped with a 4 J pendulum and a gap width of 40 mm based on ISO 179-2. The tests were performed on conditioned samples (75 mm  $\times$  10 mm  $\times$  1 mm) under standard conditions by edgewise impact testing of eight specimens for each material.

**Melt Flow Index (MFI).** The melt flow index of the PLA samples was tested based on ASTM D 1238 using a Göttfert model MPS-E melt indexer (Göttfert Werkstoff Prüfmaschinen GmbH, Buchen, Germany) at  $180^\circ\text{C}$  under an applied load of 1.2 kg. The samples were dried in a vacuum oven overnight at  $50^\circ\text{C}$  prior to the measurements.

**BPA Analysis by Gas Chromatography–Mass Spectrometry (GC–MS).** The PLA/PC samples (typically 0.6 g) were extracted and partially dissolved in dichloromethane (2 mL); methanol (8 mL) was added, which caused precipitation of the polymer. The precipitate was removed by centrifugation and the extract was analyzed by gas chromatography coupled to mass spectrometry (GC–MS) and quantified using external Bisphenol A standards.

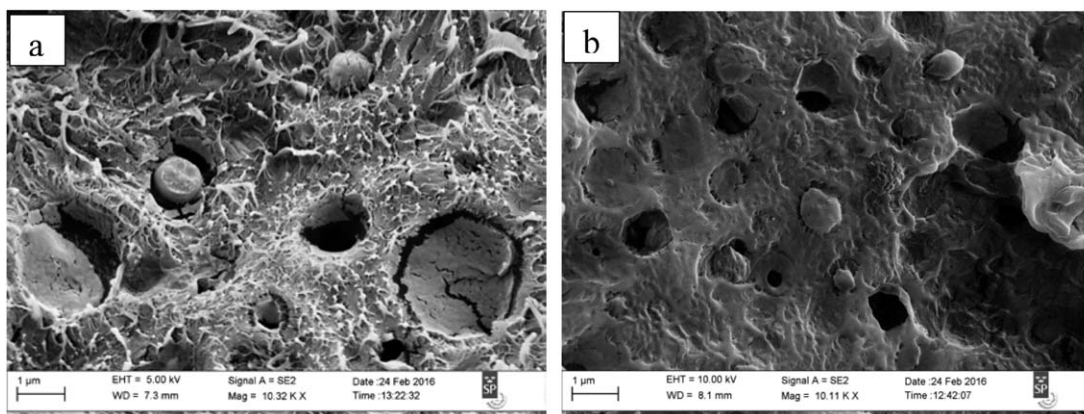
## RESULTS AND DISCUSSION

### Effects of Multiple Processing

The change in the properties of PLA/HDPE and PLA/PC blends under multiple processing compared with pure PLA is very important when assessing the environmental aspects of the blend and studying the possibility of reusing the post-production waste. The materials were evaluated after a varying number of processing steps, up to six consecutive extrusions using mechanical testing, thermal analysis, FTIR spectroscopy, and SEM. The results of the tensile tests of the PLA blends are presented in Figure 1.

Figure 1(a) shows clearly that multiple processing of the blends does not significantly affect the elastic modulus of the materials. The difference in E-modulus between the blends depended on the difference in E-modulus between pure HDPE and PC [Figure 1(a)], which have the guideline values of 800 and 2600 MPa, respectively. The corresponding guideline values for the elongation at break are 360–630% for HDPE<sup>10</sup> and about 100% for PC.<sup>11</sup> It is interesting to note that the elongation at break was significantly affected by the number of extrusions [Figure 1(b)]. However, while the elongation at break increased with the number of extrusions for the PLA/HDPE blend, the trend was reversed for the PLA/PC blend. There are two basic mechanisms that affect elongation at break. One is degradation of one or both polymers leading to chain scission and decrease in elongation at break.<sup>12</sup> The second is the increased dispersion of the dispersed phase, which means smaller domain size and lower interfacial tension<sup>13</sup> leading to increasing elongation at break.<sup>14</sup> Our results indicated that multiple processing of PLA/HDPE blend caused increased dispersion, while degradation was the dominating mechanism in the PLA/PC blend. In order to further investigate the particle size and the dispersion of PLA in HDPE, SEM images were taken on the specimens' cryofractured surfaces. Figure 2(a,b) shows the fractured surfaces of PLA/HDPE blend after one and after six extrusions.

The fractured surfaces exhibit both dispersed PLA particles and holes (voids), where PLA particles have been pulled out. Similar SEM images were reported by Balakrishnan *et al.*<sup>15</sup> even though they studied particle size of LLDPE in a PLA matrix. Using SEM images along with the instrument's software, we measured



**Figure 2.** Representative SEM images of cryofractured surfaces (a) PLA/HDPE extruded once; (b) PLA/HDPE extruded six times.

the size of many uniformly distributed particles and holes. The size of particles and holes in the blend extruded once was in the range 1.0–1.4  $\mu\text{m}$ . The corresponding values in the blend extruded six times were 0.5–0.9  $\mu\text{m}$ . This result confirms our hypothesis about a better dispersion of PLA phase in HDPE after six extrusions.

The tensile properties of the pure PLA used in this study were difficult to obtain with adequate precision because of high stiffness and brittleness of the material after repeated extrusion. The guideline values of a neat PLA are reported in the literature within a broad range, for example, for the E-modulus 0.3–5.6 GPa and for the elongation at break 1–12%.<sup>16</sup> In our case the E-modulus was close to 2 GPa and the elongation at break around 1%. For this reason, we evaluated the effects of multiple extrusions of the PLA by impact strength and MFI (Figure 3).

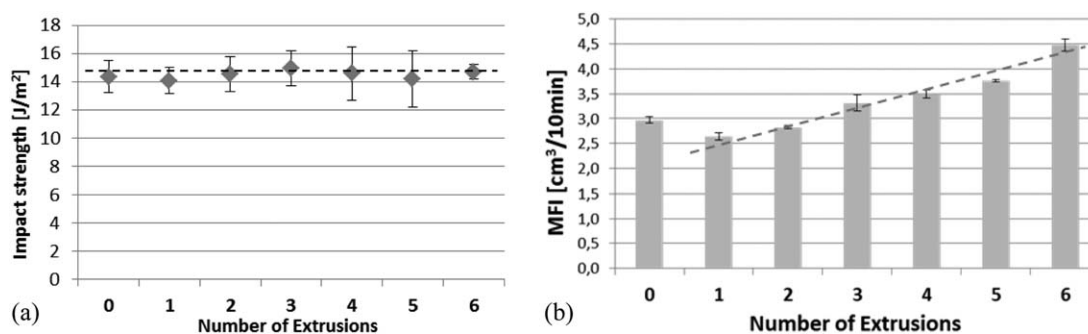
The impact strength of PLA was not affected by the number of extrusions [Figure 3(a)]. The MFI measurements were performed as an indirect measure of molecular weight. The MFI increased almost linearly with the number of extrusions [Figure 3(b)], which indicated that PLA undergoes thermal degradation during extrusion. Similar results were obtained by Pillin *et al.*<sup>17</sup> who showed that reprocessing number of PLA through injection molding has no influence on tensile modulus but at the same time, degradation of PLA during reprocessing is clearly revealed by significant decrease in viscosity and molecular weight.

The thermal properties of pure PLA and PLA blends were evaluated by DSC. The thermal parameters of the PLA part of the

materials, namely  $T_g$ ,  $T_{cc}$ ,  $T_m$ , and the melt enthalpy ( $\Delta H_m$ ), taken from the cooling and second heating runs are listed in Table I.

Thermal parameters such as  $T_m$  and the degree of crystallinity depend on the molecular weight, thermal history, and the purity of the polymer.<sup>3</sup> PLA alone does not crystallize during cooling and in particular in processes where the orientation is limited and the cooling rate is high, but it has the ability to be stress-crystallized and thermally crystallized.<sup>18</sup> Table I and Figure 4 show that the pure PLA used in this study had no crystallinity and did not cold-crystallize, but the extrusion process enabled cold crystallization to occur, which increased with the number of extrusions. The observed increase in cold crystallization indicated that shorter chains were formed during processing, which may act as nucleation centres.<sup>19,20</sup>

The DSC thermograms of the blends revealed that the components in the blends were not miscible and showed, for example, that the  $T_g$  of PLA was unaffected. However, the blending of PLA with HDPE and PC not only caused crystallization of PLA, but also led to a significant decrease in its  $T_{cc}$  (Table I) and a significant increase in  $T_m$  ( $\approx 15$  K). The results indicated that both HDPE and PC acted as nucleating agents that lower the surface free energy barrier toward nucleation and thus initiated crystallization. The effect of multiple extrusions is only observed as a decrease in  $T_{cc}$  where the effect was small in the PLA/HDPE blend ( $\approx 2$  K) but more evident in the PLA/PC blend ( $\approx 7$  K). We believe that the significant decrease in  $T_{cc}$  of PLA/

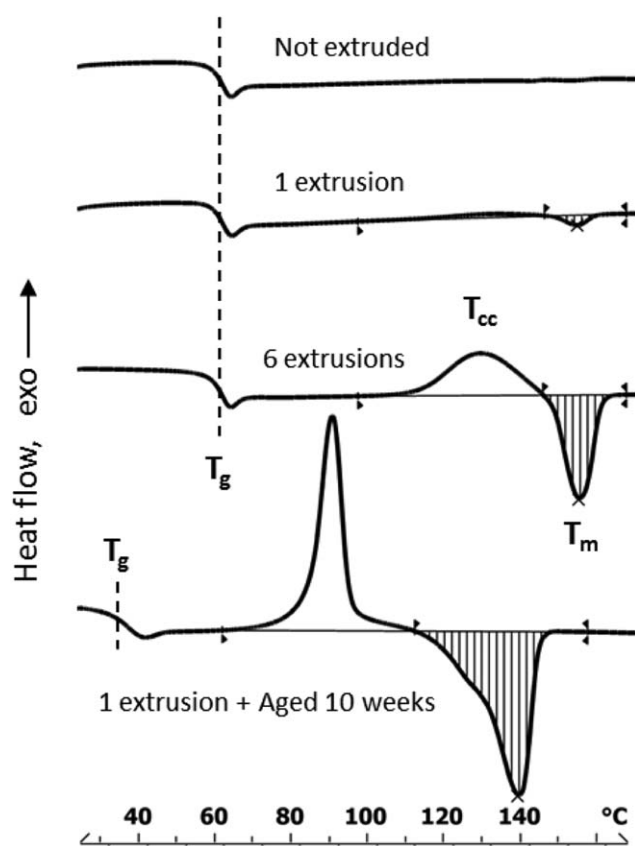


**Figure 3.** (a) Impact strength, (b) MFI versus number of extrusions.



**Table I.** Summary of the Thermal Parameters of PLA as Measured by DSC

	$T_g$ (°C)	$T_{cc}$ (°C)	$T_m$ (°C)	$\Delta H_m$ (J/g)
<b>PLA</b>				
Hot pressed	60	No peak	No peak	0
Extruded 1 time	60	Not visible	155	-1.3
Extruded 2 times	60	131	155	-8.4
Extruded 3 times	60	130	155	-14.3
Extruded 6 times	61	129	155	-17.0
<b>PLA/HDPE</b>				
Hot pressed	59	107	169	-13.4
Extruded 1 time	60	108	169	-11.8
Extruded 2 times	60	108	169	-11.8
Extruded 3 times	60	107	169	-11.9
Extruded 6 times	60	105	169	-12.7
<b>PLA/PC</b>				
Hot pressed	59	110	170	-9.1
Extruded 1 time	59	108	170	-9.0
Extruded 2 times	59	106	170	-10.0
Extruded 3 times	59	104	170	-10.9
Extruded 6 times	59	103	169	-12.0

**Figure 4.** DSC curves (second heating) of pure PLA after different numbers of extrusions and ageing (10 weeks).

PC blend was a consequence of thermal degradation of PLA during processing at high temperature (240 °C). It is generally recognized that the incorporation of high levels of PC into PLA (>50%) requires processing temperatures that are close to the thermal decomposition temperature of PLA.<sup>21</sup> Neither the  $T_g$  of PC nor the  $T_m$  of HDPE in the blends was affected by multiple extrusions as demonstrated in Figures 5 and 6.

Numbers 0–6 in Figures 5 and 6 refer to the number of extrusions.

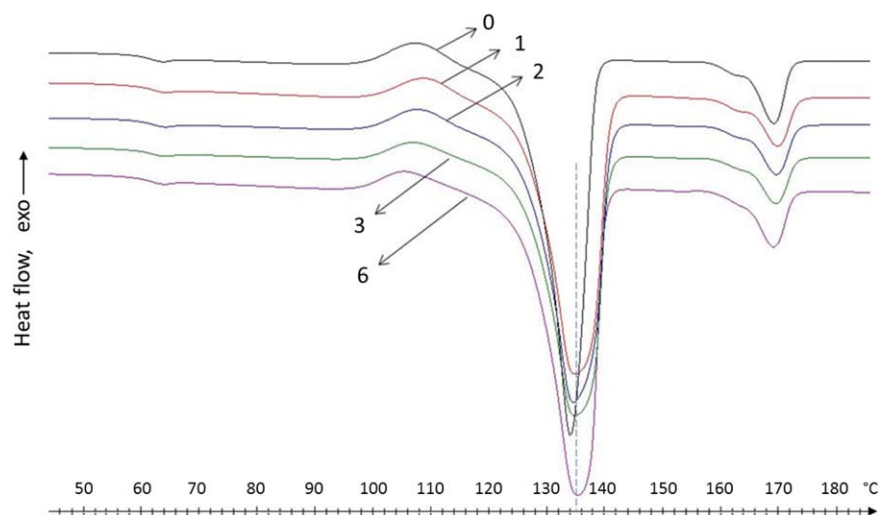
When comparing the FTIR spectra from the PLA/PC blend extruded once and six times no significant changes could be detected that could be related to the degradation of the material (see Figure 7). For comparison, a spectrum of neat PLA is shown as well.

#### Effects of Simulated Post-Consumer Recycling

The efficient and sustainable use of material resources involves the recycling of end-of-life plastic items, preferably back into a product that can then be repeatedly recycled. The simplest recycling system is closed-loop recycling, in which a single type of plastic is recycled into the same production process after the service life. To simulate post-consumer recycling, experiments were performed where a processing step was followed by simulation of a usage step through accelerated ageing, where one ageing period was estimated to correspond to one year of usage at room temperature in humid conditions. In this study, we investigated the effect of hydrothermal aging on properties and structure of PLA/PC blend only, because both components in the blend are known to be susceptible to hydrolytic degradation. The results of the simulated post-consumer recycling of the PLA/PC blend are summarized in Table II.

Table II clearly indicates that ageing in moist air caused significant degradation of the PLA part of the blend. The pure PLA was severely degraded after only one ageing cycle, thus it was not possible to measure mechanical properties, whereas the MFI value was only roughly measured and estimated to be more than 100 times higher than the unaged one. After three additional weeks of ageing (during the second ageing cycle), the pure PLA material was too brittle to handle and the ageing experiments were terminated. The thermal properties were also significantly affected by ageing as seen in Figure 4, which shows DSC curves from pure PLA after different states of processing (no, one, or six extrusions) as well as after 10 weeks ( $\approx 1.5$  ageing cycles) of ageing. The ageing of the PLA resulted in significantly lower  $T_g$ ,  $T_{cc}$ , and  $T_m$  and a major increase in the degree of cold crystallization was displayed, indicating a major reduction in molecular weight (Figure 4).

The PLA/PC blend showed improved mechanical properties and resistance to degradation compared with pure PLA. However, even one ageing cycle caused severe degradation especially of the PLA part, which was demonstrated by significantly lower  $T_g$ ,  $T_{cc}$ , and  $T_m$ . It is well known that the degradation products of PLA can reduce local pH and accelerate degradation of PC.<sup>22</sup> PC is relatively stable at high temperatures, but in contact with hot water and low pH, an acid-catalyzed, hydrolysis-induced depolymerization of PC takes place<sup>23</sup> and gives rise to the

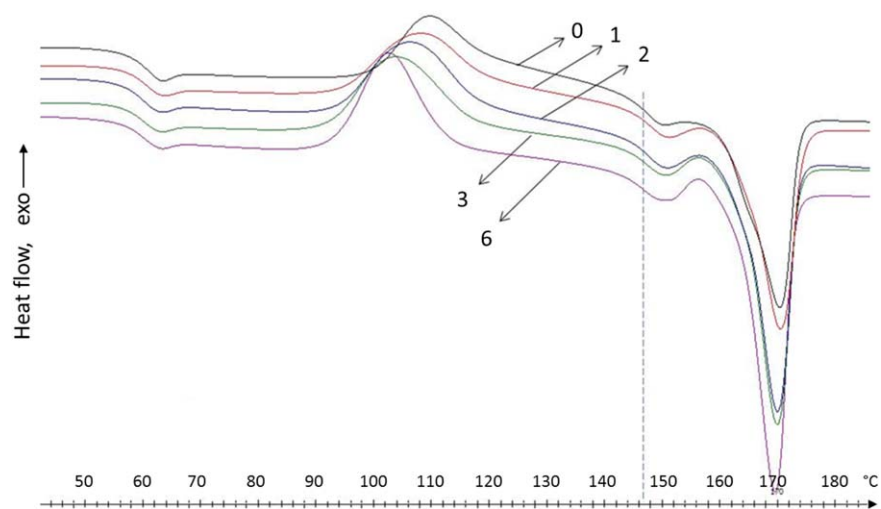


**Figure 5.** DSC thermograms of the PLA/HDPE blend after various numbers of extrusions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

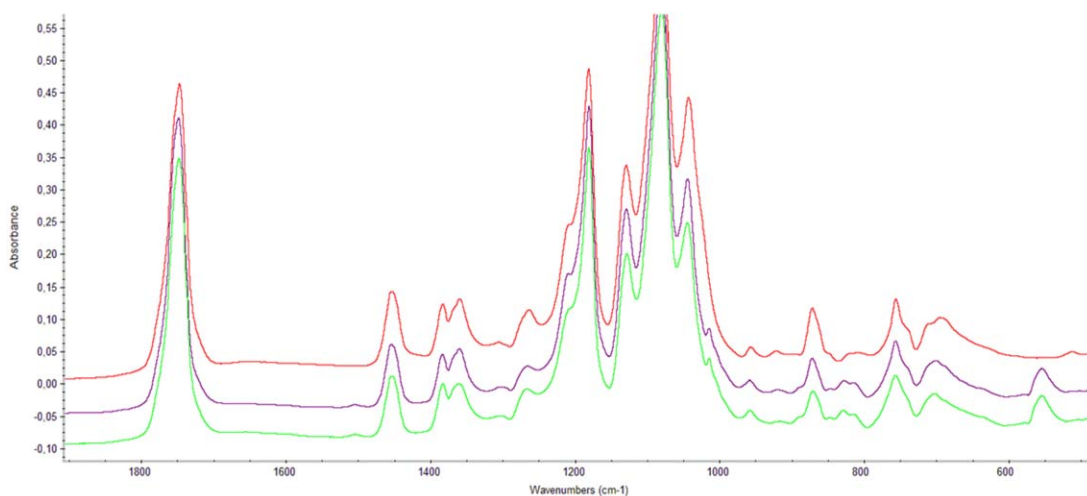
formation of monomeric Bisphenol A (BPA).<sup>24</sup> The formation of small amounts of BPA is not a health problem of the first category. The U.S. Food and Drug Administration's current perspective is that BPA is safe at the normal levels occurring in foods.<sup>25</sup> However, the presence of elevated levels of BPA is an indication of PC degradation. Therefore, analysis of BPA was performed in the PLA/PC blend by GC-MS: (a) in the original (dried) granules; (b) in the material extruded six times; and (c) in the material after one extrusion and accelerated ageing corresponding to the lifetime of 3 years at room temperature in humid conditions. The BPA content in the materials was found to be (a) 0.13, (b) 0.61, and (c) 2.3 mg BPA/g blend, which is a clear indication that the PC phase in the blend was also subjected to degradation. Furthermore, additional DSC experiments, using a higher end temperature (data not shown), revealed an additional melting peak at  $T \approx 225^\circ\text{C}$  in the aged

materials corresponding to melting of PC crystals.<sup>23</sup> This observation indicates a reduction in molecular weight of the PC phase and supports the previous findings that the PC phase in the blend was also degraded. Similar observations regarding BPA formation and PC crystallization was reported by Harris and Lee when PLA/PC-blends were subjected to humidity at higher temperatures ( $70^\circ\text{C}$ ).<sup>23</sup>

The FTIR spectra from unaged and aged (10 weeks at  $50^\circ\text{C}$  and 90% RH) PLA samples displayed many similarities. However, the aged samples showed a slightly higher intensity in the carbonyl region ( $1600\text{--}1800\text{ cm}^{-1}$ ), using the C-H asymmetric bending mode peak at  $1452\text{ cm}^{-1}$  as an internal standard.<sup>26</sup> The peak maximum was also slightly shifted toward higher wave numbers ( $1745\text{--}1751\text{ cm}^{-1}$ ). This shift to higher wave numbers is somewhat unexpected as an increase in carboxylic



**Figure 6.** DSC thermograms of the PLA/PC blend after various numbers of extrusions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



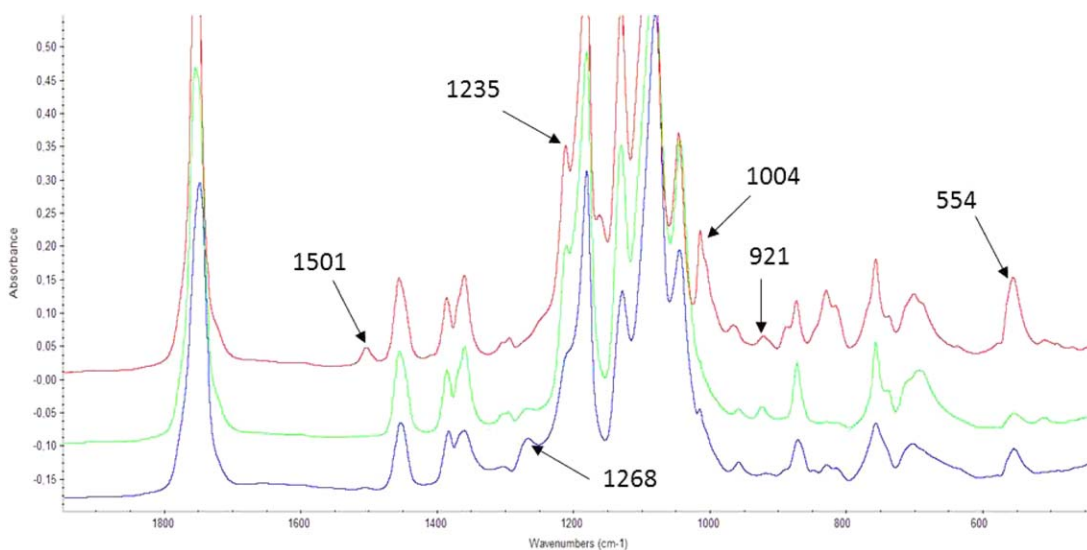
**Figure 7.** FTIR spectra of the PLA/PC blend extruded once (curve in between) and extruded six times (curve at the bottom). For comparison, spectrum of neat PLA (curve at the top). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table II.** Summary of the Effects of Post-Consumer Recycling of the PLA/PC Blend

PLA/PC	$T_g$ (°C)	$T_{cc}$ (°C)	$T_m$ (°C)	E-modulus (MPa)	Elongation at break (%)
Hot pressed	59	110	170	2270	7.3
Extruded 1 time	59	108	170	2250	8.3
Extruded 2 times	59	106	169	2260	6.1
Extruded + aged	56	105	144	2075	3.4
Extruded + aged + extruded	55	105	144	2130	1.6
Extruded + aged + aged		74	128	1505	3.5

end groups formed during hydrolysis of the ester bonds should shift the peaks to lower wave numbers.<sup>23,27</sup> However, similar observations were made by Badia *et al.* when performing multiple processing of PLA, and these were explained as indicative of

the formation of new carbonyl-linked species and indicative of molar mass reduction in the material.<sup>20</sup> There was also a noticeable difference in the 900–1000  $\text{cm}^{-1}$  region, where the aged samples displayed a major reduction in the peak at 955  $\text{cm}^{-1}$  in



**Figure 8.** FTIR spectra of the PLA/PC blend extruded once: curve at the bottom—unaged material, curve in between—after one ageing cycle, curve at the top—after two ageing cycles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

favor of the peak at  $921\text{ cm}^{-1}$  indicating an increase in crystallinity in the aged samples.<sup>26,28</sup>

The FTIR analysis of the aged PC/PLA blend revealed similar trends as for the pure PLA, with an increasing intensity of the peak at  $921\text{ cm}^{-1}$  and reduction at  $955\text{ cm}^{-1}$ , indicating an increasing crystallinity in the samples.<sup>26,28</sup> Furthermore, after the second ageing cycle, there was a noticeable increase in signal intensity at the characteristic wave numbers for PC [554  $\text{cm}^{-1}$  ( $\text{CH}_2$ ), 1004 and 1235  $\text{cm}^{-1}$  (C—O stretch), 1501  $\text{cm}^{-1}$  (C=C stretch)]<sup>29</sup> indicating a higher presence of PC (or degradation products of PC) at the surface of the aged samples. At the same time a decrease in signal intensity can be observed of the characteristic PLA peak at 1268  $\text{cm}^{-1}$  (—CO bend)<sup>30</sup> (see Figure 8).

## CONCLUSIONS

In this work, commercially available grades of pure PLA and PLA blended with PC and HDPE were investigated using methods that simulated post-processing and post-consumer recycling. Multiple processing of pure PLA did not affect impact strength or  $T_g$ , but caused crystallization and an increase in the MFI, which indicated degradation during processing. The DSC thermograms of the blends revealed that the components in the blends were not miscible. The results indicated that both HDPE and PC acted as nucleating agents that lower the surface free energy barrier toward nucleation and thus initiate crystallization of PLA. Multiple processing of the blends did not significantly affect the elastic modulus of the materials, but affected the elongation at break. However, although elongation at break increased with the number of extrusions for the PLA/HDPE blend, the trend was reversed for the PLA/PC blend. The results indicated that multiple processing of the PLA/HDPE blend caused increased dispersion and thus increased elongation at break, whereas the dominating mechanism in the PLA/PC blend was degradation, which caused a decrease in elongation at break.

Post-consumer recycling of neat PLA and PLA/PC blend was simulated by accelerated ageing in humid air followed by reprocessing. The results clearly indicated that ageing corresponding to 1 year of use caused significant degradation of PLA. Pure PLA was completely degraded after only one ageing cycle corresponding to 1 year of service at ambient conditions. Although the PLA/PC blend showed some improved mechanical properties and resistance to degradation compared with pure PLA, one ageing cycle still caused severe degradation of the PLA part and even the PC part was degraded as indicated by the formation of small amounts of BPA. The overall conclusion of the study is that blending PLA with HDPE or PC can create practical difficulties in achieving reproducibility of some properties. Besides, blending a biodegradable polymer with nonbiodegradable creates a nonbiodegradable material that should instead be suitable for mechanical recycling. However, it is a big challenge to find out how to recycle this type of blends as post-consumer materials because of the poor durability of the materials and small volumes.

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## REFERENCES

1. Soroudi, A.; Jakubowicz, I. *Eur. Polym. J.* **2013**, *49*, 2839.
2. Hopewell, J.; Dvorak, R.; Kosior, E. *Philos. Trans. R. Soc. Lond. B Biol. Sci.* **2009**, *364*, 2115.
3. Södergård, A.; Stolt, M. *Prog. Polym. Sci.* **2002**, *27*, 1123.
4. Jamshidi, K.; Hyon, S. H.; Ikada, Y. *Polymer.* **1988**, *29*, 2229.
5. Garlotta, G. *J. Polym. Environ.* **2001**, *9*, 63.
6. Hamad, K.; Kaseem, M.; Deri, F. *Asia-Pac. J. Chem. Eng.* **2012**, *7*, S310.
7. Kim, Y. F.; Choi, C. N.; Kim, Y. D.; Lee, K. Y.; Lee, M. S. *Fiber Polym.* **2004**, *5*, 270.
8. Wang, Y.; Chiao, S. M.; Hung, T. F.; Yang, S. Y. *J. Appl. Polym. Sci.* **2012**, *125*, 402.
9. ASTM F 1980, Standard Guide for Accelerated Ageing of Sterile Medical Device Packages.
10. <http://www.matweb.com/search/datasheettext.aspx?matguid=482765fad3b443169ec28fb6f9606660>
11. <http://www.matweb.com/reference/tensilestrength.aspx>
12. La Mantia, F. P. Basic Concepts on the Recycling of Homogeneous and Heterogeneous Plastics; ChemTec Publisher: Toronto, **1996**, p 63.
13. Van Puyvelde, P. V.; Moldenaers, P. *Rheol. Rev.* **2005**, 101.
14. Processing and Finishing of Polymeric Materials, Vol. 1; John Wiley & Sons, Inc. New York, **2011**, ISBN 948-0-470-88917-6, pp 120–122.
15. Balakrishnan, H.; Hassan, A.; Uzir Wahit, M. *J. Elastom. Plast.* **2010**, *42*, 223.
16. <http://plastics.ulprospector.com/generics/34/c/t/polylactic-acid-pla-properties-processing>
17. Pillin, I.; Montrelay, N.; Bourmaud, A.; Grohens, Y. *Polym. Degrad. Stabil.* **2008**, *93*, 321.
18. Battegazzore, D.; Bocchini, S.; Frache, A. *Express. Polym. Lett.* **2011**, *5*, 849.
19. Pantani, R.; De Santis, F.; Sorrentino, A.; De Maio, F.; Titomanlio, G. *Polym. Degrad. Stabil.* **2010**, *95*, 1148.
20. Badia, J. D.; Strömberg, E.; Karlsson, S.; Ribes-Greus, A. *Polym. Degrad. Stabil.* **2012**, *97*, 670.
21. [http://www.natureworkslc.com/~media/technical\\_resources/properties\\_documents/propertiesdocument\\_blends-of-ingo-with-other-thermoplastics.pdf](http://www.natureworkslc.com/~media/technical_resources/properties_documents/propertiesdocument_blends-of-ingo-with-other-thermoplastics.pdf)
22. Gorrasi, G.; Pantani, R. *Polym. Degrad. Stabil.* **2013**, *98*, 1006.
23. Harris, A. M.; Lee, E. C. *J. Appl. Polym. Sci.* **2013**, *128*, 2136.



24. The Danish Environmental Protection Agency, Migration of Bisphenol A from Polycarbonate Plastic of Different Qualities, **2015**, ISBN no. 978-87-93352-24-7.
25. Aungst, J. Center for Food Safety and Applied Nutrition (CFSAN, HFS-275) 2014, June.
26. Kister, G.; Cassanas, G.; Vert, M. *Polymer* **1997**, 39, 267.
27. Ndazi, B. S.; Karlsson, S. *Express. Polym. Lett.* **2011**, 5, 119.
28. Badia, J. D.; Santonja-Blasco, L.; Martínez-Felipe, A.; Ribes-Greus, A. *Polym. Degrad. Stabil.* **2012**, 97, 1881.
29. Ghorbel, E.; Hadriche, I.; Casalino, G.; Masmoudi, N. *Materials* **2014**, 7, DOI: 10.3390/ma7010375
30. Nikolic, L.; Ristic, I.; Adnadjevic, B.; Nikolic, V.; Jovanovic, J.; Stankovic, M. *Sensors* **2010**, 10, 5063.