Biodegradable Blend Based on LDPE/Starch with Agriculture Applications

MARIA RAPA*, ELENA GROSU¹, ZINA VULUGA², ANDREIANA SCHEAU, CRISTIAN STANESCU
¹ S.C. INCERPLAST S.A., 23 Ziduri Mosi Str., 021203, Bucharest, Romania
² ICECHIM, 202 Independence Str., 060021, Bucharest, Romania

A biodegradable blend based on low-density polyethylene (LDPE) and 36 % starch that can be used for horticultural application was studied. The mechanical properties and the processing by molding injection were also studied. It is found that the starch helps to increase surface area on which the microorganism can attach the polymer matrix. The increase in the carboxyl index, which indicates the concentration of carboxyl blend, with time, also indicates the progress of biodegradation. Although this type of blend is not completely biodegradable it is preferred to those completely biodegradable which are expensive and with many processing problems.

Keywords: biodegradation, starch, polyethylene, blend, application

Conventional petrochemical-based plastics (e.g. polyethylene, polypropylene etc.) are not easily degraded in the environment due to their high molecular weight and hydrophobic characters. These synthetic polymers persist for many years after disposal [1].

Polyethylene materials are known to be sensitive to thermal oxidation, due to the impurities generated during their manufacture at high temperatures. Despite this fact, their slow abiotic oxidation rate means that they should be classed as non-biodegradable polymers [2-3]. A possible solution to reduce the considerable amount of polyolefin wastes, would be to induce a certain level of biodegradability by adding biodegradable additives in the form of master-batches [4] and/or pro-oxidants [5].

The most commonly used additives are based on starch and other components [6 - 8]. Starch has gained considerable interest because it is inexpensive, available in large amounts from different sources and has provided a viable alternative to replace synthetic polymers, decreasing in consequence the environmental pollution [9 - 12]. Plastic materials that are formed from starch-based blends may be injection molded, extruded, blown, or compression molded.

It was found that the mixing of corn starch with polymer, lead to the biodegradability of the starch-polyethylene composites evaluated by weight loss, resulting CO₂ [13].

Current requirements regarding environmental protection have become of great importance in our society, so it feels more and more interest in increasing industrial use of renewable resources [14, 15].

Each year the nursery/landscape, greenhouse, vegetable industries and end users discard millions of non-degradable pots with which plants were grown. This creates a waste disposal problem that is detrimental to the environment and is costly in landfill fees.

The development of biodegradable pots that degrade over a specified time period under specific conditions (and also maintain its integrity and performance throughout the season) would eliminate the need to remove the pots at the end of the growing season. Furthermore biodegradable pots will avoid transplanting damages of plants, thus reducing transplant stress.

It is known biodegradable pots use a state of the art composite made of ceramic, peat or agricultural residues mainly bamboo pulp (Enviroarc, Jiffy).

In this article we studied the properties of the biodegradable blend of starch with LDPE comparative with standard LDPE, and the optimum temperatures for injection molding to obtain biodegradable pots.

Experimental part

Material and method

Biodegradable blend based on LDPE and starch, 36 % content of starch, was obtained by twin screw extrusion technology, in the shape of granules. For the compatibilization of the filler with polymer matrix, coupling agents were used: polyethylene-g-maleic anhydride copolymer (PE-g-AM) and vinyl polyacetat-alt-maleic anhydride (PAcV-AM) copolymer [16].

Mechanical properties such as tensile strength, elongation at break were tested by using injection molded specimens in the following conditions: temperature profile: 160/170/1800°C ± 5°C; injection pressure (1400 ± 50) daN/cm²; injection rate: 5 cm/s; injection time: 5 s.; cooling time: 3 min; cooling time: 40 min; pressure: 250 bar.

The optical microscopy, UV/VIS and IR transmittance and weight loss of buried blend testing were performed on films having an average thickness of ~50μm. Films were obtained by pressing in the following conditions: temperature: (170 ± 5)°C; preheat time: 8 min; pressing time: 3 min; cooling time: 40 min; pressure: 250 bar.

In order to obtain the biodegradable plant pots, the granules are dried in the oven at 80°C, for 2 h, before being processed by molding injection technology.

Application of blend based on LDPE and starch

Bags, mulch films, wrapping film, paper lamination, net, cutlery, flower pots, boxes, controlled release fertilizers materials, trays for food and non-food articles are some examples of starch-based materials made using the existing thermoplastic technology [17 - 19].

Figure 1 shows the pots for transplanting plants by molding injection technology. Injection molding experiment was carried out using a reciprocating-screw...
injection molding machine (KUASSY 150) with a maximum clamping of 530 kN. Machine settings are shown in Table 1. The mold was opened and pots were cooled at room temperature. The red pots by adding silica colorant during the molding process were obtained.

### Table 1

**RECIPIROCATING-SCREW INJECTION MOLDING MACHINE SETTINGS**

<table>
<thead>
<tr>
<th>Setting</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection pressure</td>
<td>800 kN/cm²</td>
</tr>
<tr>
<td>Injection pressure time</td>
<td>10 s</td>
</tr>
<tr>
<td>Barrel temperature profile</td>
<td>20 – 170 - 180 - 190 °C</td>
</tr>
<tr>
<td>Feed – zone 1- zone 2 – nozzle</td>
<td></td>
</tr>
<tr>
<td>Screw speed</td>
<td>135 rpm</td>
</tr>
<tr>
<td>Cooling time</td>
<td>15 s</td>
</tr>
</tbody>
</table>

They were obtained in the following sizes as shown in the table 2.

### Table 2

**SPECIFICATIONS OF DIMENSIONS**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>1.8 mm</td>
</tr>
<tr>
<td>Volume</td>
<td>165 cm³</td>
</tr>
<tr>
<td>Weight</td>
<td>32 g</td>
</tr>
<tr>
<td>Depth</td>
<td>74 mm</td>
</tr>
<tr>
<td>OD at top</td>
<td>73 mm</td>
</tr>
<tr>
<td>OD at base</td>
<td>53 mm</td>
</tr>
</tbody>
</table>

In order to characterize the biodegradable blend comparative with standard LDPE the following tests are used: the melt flow index, the density, the hardness Shore, the tensile strength and elongation at break, the water absorption, the optical microscopy, the optical transmittance and the weight loss of buried blends.

Prior to mechanical measurements, the samples were conditioned at (50 ± 5) % relative humidity for 48 h at (23 ± 1) °C, in a climatic chamber type BTH80/-20 according to ISO 291.

The melt mass-flow rate (MFR) is performed according to ISO 1133, Method A, the nominal load is 2.16 kg, and the test temperature is 190 °C.

The density is performed according to ISO 1183, Method A, on the cut-off the extrude, conditioned in an oven, at 100 °C, for 30 min.

Measurements of tensile properties, such as tensile strength and elongation at break were performed on a DINAMOMETER FP 10/1, according to the ISO 527-3. Five replicates were tested for each sample, and average values of the elongation at break, tensile strength were determined. The tensile strength is the maximum load divided by the original cross sectional area.

Specimens for measuring water absorption were in the form of disc 50 mm (1 mm thickness) following the ISO 62, Method 1 – Determination of water content absorbed after immersion in water at 23 °C. Test specimens were dried in an oven at (50 ± 2) °C for (24 ± 1) h, cooled in the desiccator and then immediately weighed to the nearest 0.1 mg (this weight designated as mass \( m_f \)). Thereafter, the conditioned test specimens were immersed in distilled water, maintained at (23 ± 1) °C, for (24 ± 1) h test period. After this period, they were removed from the water, gently blotted with tissue paper to remove excess water on the surface, immediately weighed to the nearest 0.1 mg (designated as mass \( m_i \)). Each \( m_f \) was an average value obtained from three measurements. The percentage increase of water (in weight) was calculated to the nearest 0.01% as follows:

\[
c = \frac{(m_f - m_i)}{m_i} \times 100
\]

where \( c \) is the final percentage increase in weight of the tested specimens.

Hardness Shore is performed with the VEB Hardness.

Biodegradability of the biodegradable blend comparative with standard LDPE was assessed by evaluating weight loss of blend over time in a soil with the \( pH \) (1:10) in water with \( pH \) 7.5. Three specimens of (30 mm x 30 mm x 1 mm) from each sample were weighed and then buried in boxes of soil. Soil was maintained at 20 % moisture in weight and specimens were buried at a depth of 15 cm, following the EN ISO 846. The buried samples were removed from the soil once a week, washed in distilled water, dried in an oven at (50 ± 8) °C for 24 h and equilibrated in a desiccator for at least a day, before being weighed and then returned to the soil. Dried films were weighed to calculate the weight loss.

The evaluation of the weight loss was performed by using the formula:

\[
\text{Weight loss, \%} = \frac{(m_f - m_i)}{m_i} \times 100
\]

where:
- \( m_f \) is the final weight of the tested samples;
- \( m_i \) - the initial weight of the tested samples.

This ratio is, generally, negative due the weight loss.

The surface morphology of biodegradation of the polymer specimen was photographed by MOTIC DMW B-223 ASC Microscopy with 40X magnification.

The optical transmittance of the films in the wavelength range of 200–800 nm was measured by using a UV/VIS HELIOS ALPHA Spectroscope, according to the Beer–Lambert law to give percent light transmittance for the films.

The FT-IR spectra were recorded on a FTLA2000-104 Spectrometer, in the range 600 cm⁻¹ - 4000 cm⁻¹, slot 2.5 and resolution 4 cm⁻¹. Based on the FT-IR spectra taken for standard LDPE, LDPE/starch blend and LDPE/starch after one month exposure in soil, hydroxyl indices were calculated according to relationship (3) [20]:

\[
I_{C,OH} = \frac{A_{3350}}{A_{1475}}
\]

where:
- \( A_{3350} \) is the absorbance assigned to the group -OH;
- \( A_{1475} \) - the reference absorbance band attributed to deformation vibration (CH2).
Results and discussion

The physical properties of LDPE/starch blend versus standard LDPE are shown in table 3.

Melt index

The melt mass-flow rate (MFR) depends on the rate of shear, and the results obtained correspond with the rheological behaviour of thermoplastics at processing by molding. By adding starch, the viscosity of blend decreased comparative with pure LDPE.

Tensile property

The data shown in table 3 indicate that the tensile strength and elongation at break decrease slightly in the LDPE/starch blend comparative with standard LDPE. In general it is known that a better dispersion of the starch in the thermoplastic matrix leads to better mechanical properties.

Generally speaking, the hydrophobic LDPE is not compatible with hydrophilic starch. The starch granule is highly hydrophilic, containing hydroxyl groups on its surface, whereas LDPE is mostly non-polar. Therefore, the strong interfacial bonds such as hydrogen bonds between starch and LDPE are not formed and the mechanical properties of the LDPE/starch blend were rather poor.

Melting temperature

The melting temperature of biodegradable blend increased with ~ 50% than standard LDPE, this means a decreased of crystallization of biodegradable blend. This

<table>
<thead>
<tr>
<th>Property</th>
<th>U.M.</th>
<th>Test</th>
<th>Standard Value</th>
<th>LDPE/starch blend Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt mass-flow rate (MFR)</td>
<td>g/10</td>
<td>SR EN ISO 1133-2005 Method A</td>
<td>0.321</td>
<td>0.966</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>MPa</td>
<td>SR EN ISO 527-2-2000</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>Elongation</td>
<td>%</td>
<td>SR EN ISO 518-3-1-2004</td>
<td>530</td>
<td>70</td>
</tr>
<tr>
<td>Density</td>
<td>g/cm³</td>
<td>SR EN ISO 1183-1-2004 Method A</td>
<td>0.9180</td>
<td>1.0320</td>
</tr>
<tr>
<td>Melting temperature, Tm</td>
<td>°C</td>
<td>Boëtius Microtable</td>
<td>118 – 120</td>
<td>150 – 180</td>
</tr>
<tr>
<td>Crystallization temperature, Tc</td>
<td>°C</td>
<td>Boëtius Microtable</td>
<td>105</td>
<td>90</td>
</tr>
<tr>
<td>Shore Hardness</td>
<td>%</td>
<td>SR EN ISO 868-2003 Method 1</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>Water absorption</td>
<td>%</td>
<td>SR EN ISO 62-2004 Method 1</td>
<td>0.019</td>
<td>1.650</td>
</tr>
</tbody>
</table>
The data shown in figure 3 reveals that the standard LDPE remains unchanged, even after 3 months, and no weight loss is noticed. Instead, the concentrate based on LDPE/starch blend records an increasing weight loss for three months. This weight loss for LDPE/starch blend is attributed to the starch consumption by microorganisms, which should result in the surface of the films being full of holes. The photomicrographs of the biodegradable blend made initially, after two months and three months of exposure in the soil are presented in figure 4.

The biodegradation of LDPE/starch blend suggests that microbes consume starch as a food source and create pores in the materials, leading to an increase in the surface area of polyethylene matrix and providing susceptible groups for its biodegradation [22]. The water absorption of LDPE/starch blend is another cause of degradation. The water absorption on the material allows the microorganisms to grow and utilize the material as a carbon source. It was reported that in the soil, water diffused into the polymer sample, causing swelling and enhancing biodegradation [23].

The only advantage in the incorporation of starch into LDPE is that after starch consumption the blend ends up in a form full of holes. This offers an increased surface area on which the microorganisms can attack the polymer matrix.

Though the exact nature of the process undergone by starch was not determined, several of the processes that may compete during the degradation in soil are the following: crosslinking, hydrolysis due to the bonding α(1-4) of amyllose and amylopectin to produce cycloextrins, the elimination of amyllose units, which increases the glass transition temperature of the material, etc. [24].

Optical transmittance

The light transmittance of the LDPE/starch blend achieved 39% at 800 nm, instead the pure LDPE shows a maximal light transmittance at 88% for the same wavelength (fig. 5). These data regarding to films transmittance are useful to obtain foils for agriculture area, knowing that the plants perceive radiation between UV 290-400 nm domain and far IR above 800 nm [25].
The FT-IR spectra of standard LDPE and LDPE/starch blend initially and after one month of exposure in the soil are presented in figure 6 and figure 7. From FT-IR spectra of standard LDPE (fig. 6) were observed following intense bands: at 731 cm\(^{-1}\) attributed to rocking CH\(_2\), at 1473 cm\(^{-1}\) attributed to bending CH\(_2\) and at 2924 cm\(^{-1}\) attributed to stretching CH.
Also, the FT-IR spectra of LDPE/starch blend (fig. 7) shows a broad band at 3600 cm$^{-1}$-3000 cm$^{-1}$, in which the absorption band is related to free hydroxyl groups of pure starch, at 1019 cm$^{-1}$ and 1156 cm$^{-1}$, attributed to C-O-C bond stretching, and the peak near 1019 cm$^{-1}$ was a characteristic peak of the anhydro-glucose ring O-C stretch [26]. The absorption band at 2930 cm$^{-1}$ refers to the C-H stretching present in the starch. Interestingly, the peak at 1726 cm$^{-1}$, attributed to the -C=O groups of the LDPE/starch blend has a higher concentration of OH groups which are promoters of oxygen. Therefore LDPE/starch blend has a higher degradation rate than the standard LDPE after exposure in soil.

Figure 8 shows growth of the hydroxyl absorption band at 3350 cm$^{-1}$ which leads to an increase in the hydroxyl index. This suggests that LDPE/starch blend after one month exposure in soil reveals a higher hydroxyl index compared to the control sample LDPE, indicating a higher rate of formation of OH units than the standard LDPE. LDPE/starch blend has a higher concentration of OH groups and 36 % starch content were investigated by mechanical, biodegradability and optical tests.

Conclusions
The properties of biodegradable blend based on LDPE and 36 % starch content were investigated by mechanical, biodegradability and optical tests.

The biodegradation was affected by the LDPE/starch blend through apparition of pores, holes in the material that leads to an increased surface area though the microorganisms can attack the polymer matrix.

FT-IR spectra were intended to show the increasing hydroxyl index to evaluate the sample degradation based on LDPE and starch than the standard LDPE.

Biodegradable LDPE/starch blend was processed by conventional injection molding technology to have applications in horticultural plant pots.

References
4. GRUFFIN, G.J.L., Chemistry and technology of biodegradable polymers. Glasgow, Blackie, 1994
15. ZOU, J., IJU, C., ELLASSON, B., Modification of starch by glow discharge plasma, Carbohydrate Polymers, 55, 2004, p. 23

Manuscript received: 10.02.2010