Biodegradable Blend Based on LDPE/Starch with Agriculture Applications

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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 attack 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 CO_2 [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: 160/170/180^{0}C ± 5°C; injection pressure (1400 ± 50) daN/cm^2; injection rate: 5 cm/s; injection time: 5 s.; cooling time: 10 s.

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^{0}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

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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
RECIPROCATING-SCREW INJECTION MOLDING MACHINE SETTINGS

Reciprocating-screw injection molding machine settings	
Injection pressure	800 kN/cm^2
Injection pressure time	10 s
Barrel temperature profile: feed – zone 1- zone 2 – nozzle	20 – 170 - 180 – 190 ^{0}C
Screw speed	135 rpm
Cooling time	15 s

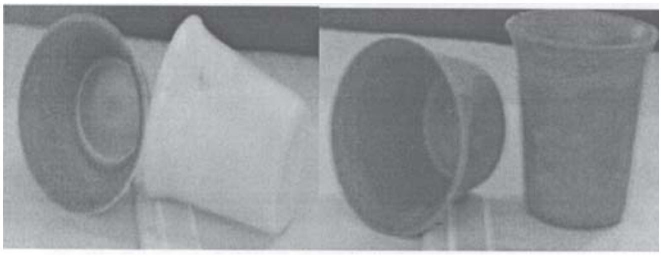


Fig. 1. Pots by molding injection technology

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

Table 2
SPECIFICATIONS OF DIMENSIONS

Specifications of dimensions	
Thickness	1.8 mm
Volume	165 cm3
Weight	32 g
Depth	74 mm
OD at top	73 mm
OD at base	53 mm

Characterization

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) ^{0}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 ^{0}C.

The density is performed according to ISO 1183, Method A, on the cut-off the extrudate, conditioned in an oven, at 100 ^{0}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^{0}C. Test specimens were dried in an oven at (50 ± 2) ^{0}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_1). Thereafter, the conditioned test specimens were immersed in distilled water, maintained at (23 ± 1)^{0}C, for the (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_2). Each m_1 was an average value obtained from three measurements. The percentage increase of water (in weight) was calculated to the nearest 0.01% as follows:

$$c\,\% = \frac{(m_2 - m_1)}{m_1} x100 \qquad (1)$$

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 *p*H (1:10) in water with *p*H 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) ^{0}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:

$$Weight\ loss,\ \% = \frac{(m_f - m_i)}{m_i} x100 \qquad (2)$$

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]:

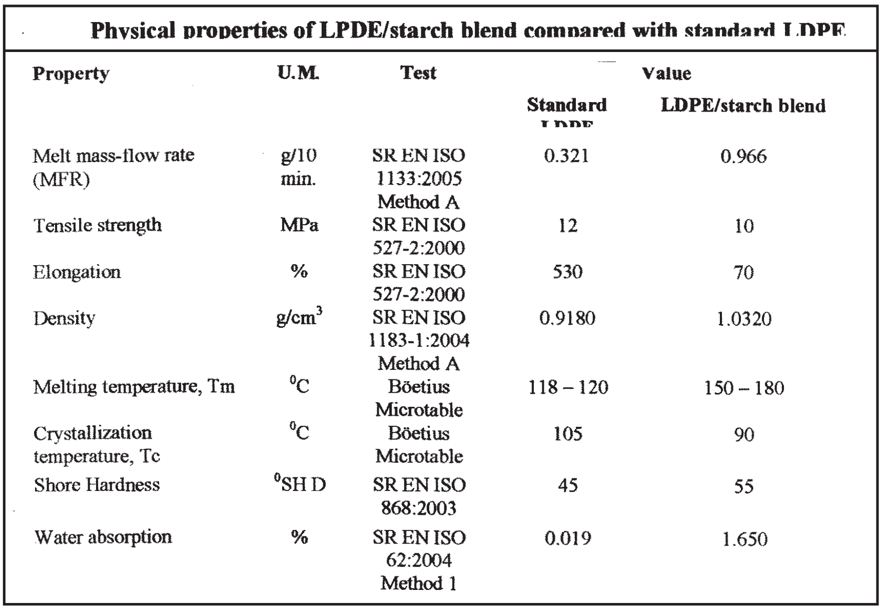
$$I_{C\text{-}OH} = \frac{A_{3350}}{A_{1475}} \qquad (3)$$

where:

A_{3350} is the absorbance assigned to the group -OH

A_{1475} - the reference absorbance band attributed to deformation vibration (CH2).

Table 3
PHYSICAL PROPERTIES OF LDPE/STARCH BLEND COMPARED WITH STANDARD LDPE



Physical properties of LPDE/starch blend compared with standard LDPE

Property	U.M.	Test	Value	
			Standard LDPE	LDPE/starch blend
Melt mass-flow rate (MFR)	g/10 min.	SR EN ISO 1133:2005 Method A	0.321	0.966
Tensile strength	MPa	SR EN ISO 527-2:2000	12	10
Elongation	%	SR EN ISO 527-2:2000	530	70
Density	g/cm^3	SR EN ISO 1183-1:2004 Method A	0.9180	1.0320
Melting temperature, Tm	^{0}C	Böetius Microtable	118 – 120	150 – 180
Crystallization temperature, Tc	^{0}C	Böetius Microtable	105	90
Shore Hardness	^{0}SH D	SR EN ISO 868:2003	45	55
Water absorption	%	SR EN ISO 62:2004 Method 1	0.019	1.650

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.

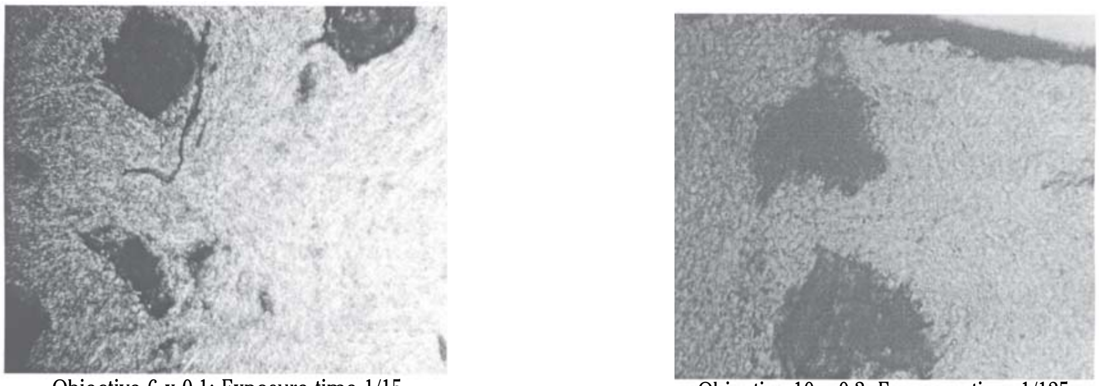
Tensile property

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.

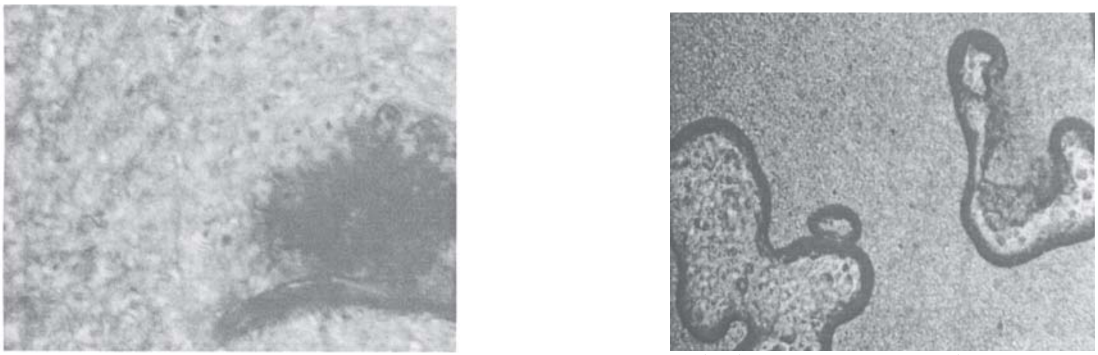
Melting temperature

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



Objective 6 x 0,1; Exposure time 1/15
a

Objective 10 x 0,3; Exposure time 1/125
b



Objective 40 x 0,65 ; Exposure time 1/15
c

Objective 10 x 0,6; Exposure time 1/60
d

Fig. 2. Optical microscopy by Microtable Böetius
a), b), c) before melting; d) after melting

fact will show a positive effect for biodegradable process that is confirmed in amorphous zones. In figure 2 (a, b, c) the optical images for biodegradable LDPE/starch structure before to exposure at soil are shown. Figure 2 (d) shows the structure of blend after melting at 180 ^{0}C.

In the LDPE/starch blend, the matrix is LDPE and the dispersed phase is starch. Figure 2 shows a poor dispersion between two phases: thermoplastic matrix as continuous phase and filler.

Water absorption

It can be observed that the water absorption of the LDPE/ Starch blend was higher than of the standard LDPE. This result means that the blend could absorb more water and microorganisms in soil water, and thus leading to a more biodegradability.

The percentage water absorption increased due to the starch content. These phenomena were similar to the results from [21]. By studying blends of starch and polyethylene, to researchers deduced that the marked increase in water absorption was probably caused by the increased difficulty in forming polymer chain arrangements as the starch hindered the movements of the polymer segments, and also that the hydrophilic character of starch led to poor adhesion with the hydrophobic polyethylene.

Biodegradation under soil

The weight loss during soil burial up to 3 months is presented in figure 3.

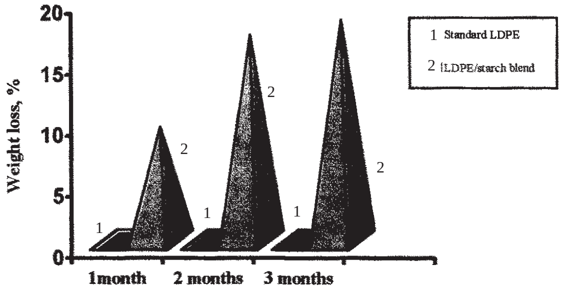


Fig. 3. Weight loss under soil

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 microorganism, which should result in the surface of the films being full of holes. The photomicrographies of the biodegradable blend made initially, after two months and tree 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 micro-organisms 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 micro-organisms 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 amylose and amylopectin to produce cyclodextrins, the elimination of amylose 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].

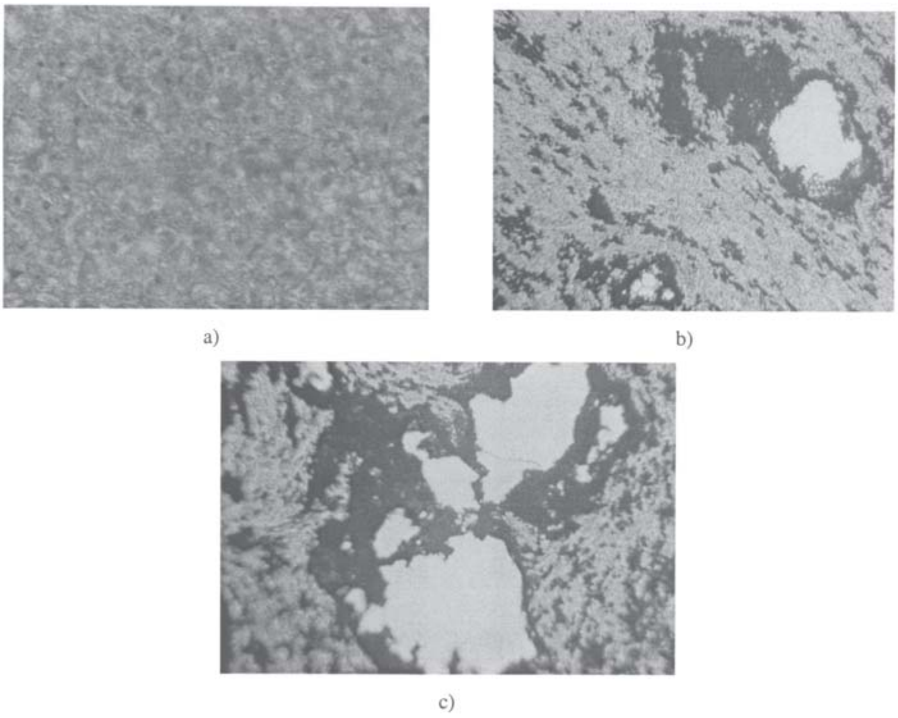
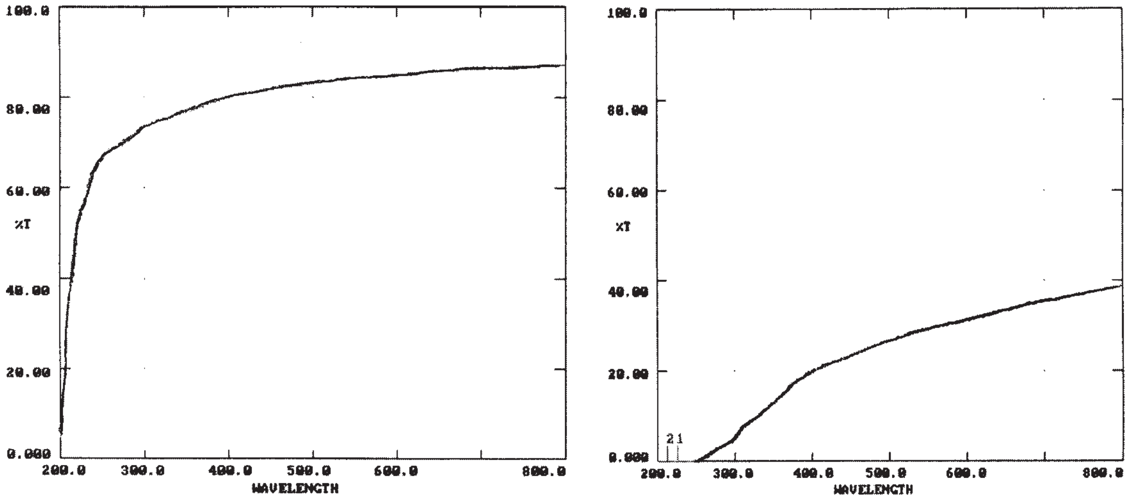

a)
b)
c)

Fig. 4. The behavior at biodegradability for LDPE/starch blend
a) Initial; b) After 2 months c) After 3 months



a) b)

Fig. 5. Light transmittance by UV/VIS spectrometer
a) Standard LDPE; b) LDPE/starch blend

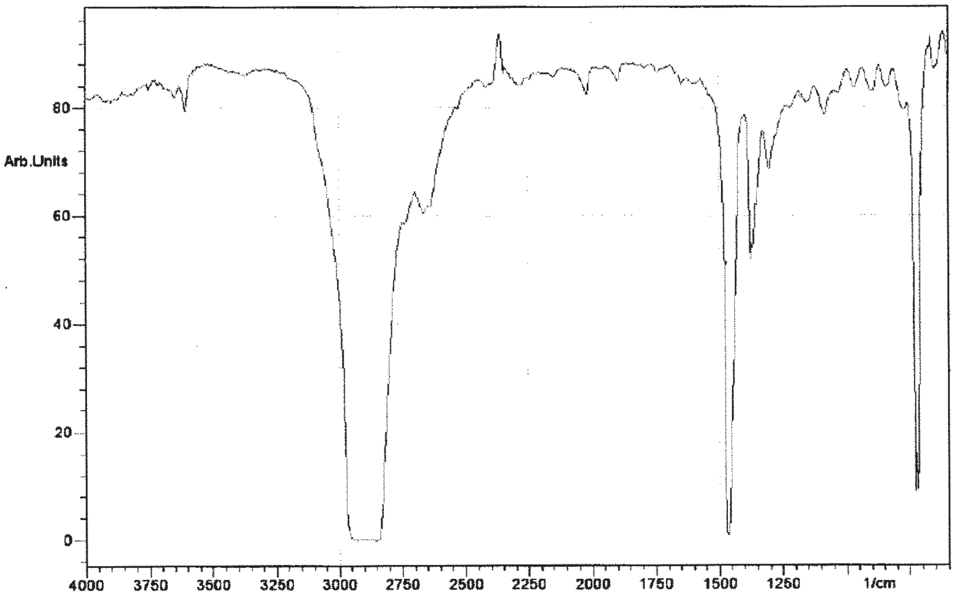


Fig. 6. FT-IR spectra of LDPE pure

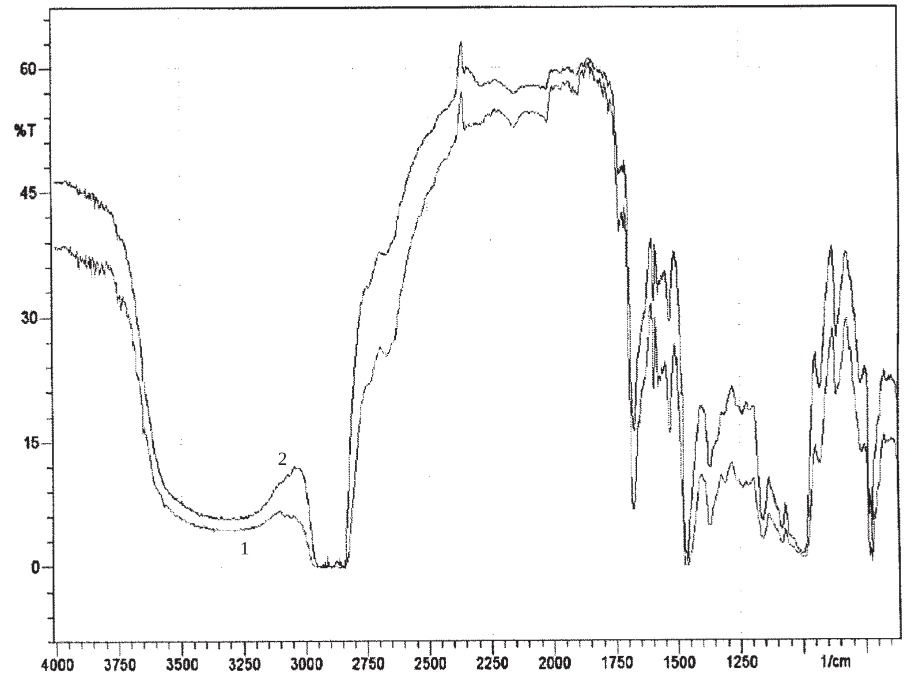


Fig. 7. FT-IR spectra of LDPE/starch blend
1- LDPE/starch blend; 2 - LDPE/starch blend, after one month exposure in soil

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 731cm^{-1}, attributed to rocking CH$_2$, at 1473 cm^{-1} attributed to bending CH$_2$ and at 2924 cm^{-1} attributed to stretching CH.

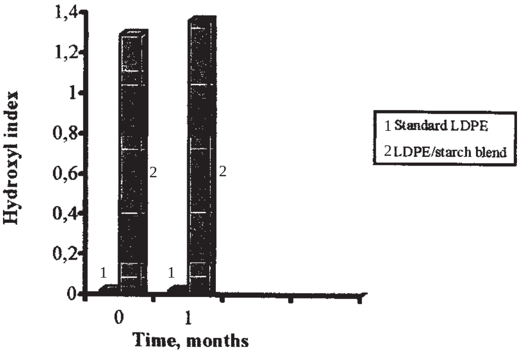


Fig. 8. Hydroxyl index of LDPE and LDPE/starch blend after one month exposure in soil

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, implying a good miscibility.

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 which are promoters of oxygen. Therefore LDPE/starch blend has a higher degradation rate than the standard LDPE after exposure in soil.

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

1. GROSS, A. R., KALRA, B. Biodegradable polymers for the environment, Science, **297**, 2002, p. 803

2. OHTAKE, Y., KOBAYASHI, T., ASABE, H., MURAKAMI, N., ONO, K., Oxidative degradation and molecular weight change of LDPE buried under bioactive soil for 32-37 years. J. Appl. Polym. Sci., **70,** 1998, p. 1643

3. KHABBAZ, F., ALBERTSSON, A., KARLSSON, S., Chemical and morphological changes of environmentally degradable polyethylene films exposed to thermo-oxidation. Polym. Degrad. Stab., **63,** 1999, p. 127

4. GRIFFIN, G.J.L., Chemistry and technology of biodegradable polymers. Glasgow, Blackie, 1994

5. ERLANDSSON, B., KARLSSON, S., ALBERTSSON, A.C., The mode of action of corn starch and a pro-oxidant system in LPDE: Influence of thermo-oxidation and UV-irradiation on the molecular weight changes, Polym. Degrad. Stab., **55**, 1997, p. 237

6. RAMIS, X., CADENATO, A., SALLA, J.M., MORANCHO, J.M., VALLE´S, A., CONTAT, L., RIBES, A., Thermal degradation of polypropylene/starch-based materials with enhanced biodegradability, Polym. Degrad. Stab., **86**, 2004, p. 483

7. BURGESSCASSLER A., IMAM S.H., GOULD J.M., High-molecular weight amylase activities from bacteria degrading starch-plastic films, Appl. Environ. Microbiol., **57**, 1991, p. 612

8. WOOL R.P., RAGHAVAN D., WAGNER G.C., BILLIEUX S., Biodegradation dynamics of polymer-starch composites, J. Appl. Polym. Sci., **77**, 2000, p. 1643

9. SHOGREN, R.L., Starch: properties and materials applications. In: Kaplan DL, editor. Biopolymers from renewable resources, Medford, USA: Springer, 1998

10. MOHANTY, A.K., MISRA, M., HINRICHSEN, G., Biofibres, biodegradable polymers and biocomposites: an overview. Macromol. Mater. Eng., **276-277**, 2000, p. 1

11. RATNAYAKE, W.S., HOOVER, R., WARKENTIN, T., Pea starch: composition, structure and properties a review. Starch/Sta¨ rke, **54**, 2002, p. 217-34

12.DIMONIE, D., RADOVICI, C., SERBAN, S., TARANU, A., VASILIEVICI, G., Mat. Plast., **44**, no. 2, 2007, p. 148

13.SATYANARAYANA, K.G., Biodegradable composites based on lignocellulosic fibers, International Conference on Advanced Materials and Composites (ICAMC-2007), Oct 24-26, 2007, p. 12

14. RICHARDSON, S., GORTON, L., Characterisation of the substituient distribution in starch and cellulose derivatives, Analytica Chimica Acta, **497**, 2003, p. 27

15. ZOU, J. J., LIU, C. J., ELIASSON, B., Modification of starch by glow discharge plasma, Carbohydrate Polymers, **55**, 2004, p. 23

16. BERCU, C., VULUGA, Z., IORGA, M., FLOREA, D., POP, S., Photodegradability of Biodegradable LDPE Based Composites, J., of Colloid and Surface Chemistry, **7**, Nr. 1, 2007, p. 45

17. BASTIOLI, C., Polym. Degrad. Stab., **59**, 1998 p. 263

18. LORKS, J., Polym. Degrad. Stab., **59,** 1998, p. 245

19. DILARA, P. A., BRIASSOULIS, D., Degradation and stabilization of low-density polyethylene films used as greenhouse covering materials, Journal of Agricultural Engineering Research, **76**, 2000, p. 309

20. J. LACOSTE, D.J. CARLSSON, J. Polym. Sci., Part. A, Polym. Chem., **30**, 1992, p. 493

21. BIKIARIS, D., PANAYIOTOU, C., J. Appl. Polym. Sci., **70,** 1998, p. 1503

22. THAKORE, I.M., IYER, S., DESAI, A., LELE, A., DEVI, S., J. Appl. Polym. Sci., **74,** 1999, p. 2791

23. CHANDRA, R., RUSTGI, R., Polym. Degrad. Stab., **56**, 1997, p. 185

24. RAMIS, X., Polym. Degrad. Stab., **86**, 2004, p. 483

25. GROSU, E., NEMES, E., RÂPĂ, M, CIOFU, R., PRODĂNEL, A., Mat. Plast., **45**, no. 1, 2008, p. 74

26. FANG, J.M., FOWLER, P.A., TOMKISON, J., Hill CAS. Carbohydr. Polym., **47**, 2002, p. 245

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