BIODEGRADABILITY DETERMINATION OF VEGETAL ORIGINATED PACKAGING MATERIALS UNDER CONTROLLED COMPOSTING CONDITIONS

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Abstract. *The paper presents methodologies for the determination of corn starch packaging ultimate biodegradability under controlled composting conditions by measurement of the amount of carbon dioxide evolved and the degree of packaging disintegration at the end of the test. The composting takes place in an installation with controlled temperature, aeration and humidity.*

Keywords: compost, biodegradability, vegetal products

INTRODUCTION

In the last years synthetic polymers are started to be replaced by biodegradable materials in many packaging applications despite to their low cost, low density, resistance to corrosion, suitable physical and mechanical properties and ease of processing, mostly due to their adverse environmental effects, negative impact on wildlife and especially aquatic organisms and their high volume disposed of in landfills [1].

Natural polymeric materials such as polysaccharides (starch, cellulose), proteins and triglycerides (vegetable oils) are biodegradable, therefore can play a significant role in solving environmental problems caused by the use of synthetic polymeric materials. Thus, the industrial scale development of eco-friendly materials and the implementation of new technologies to produce biodegradable packaging materials from renewable natural resources receive increasing attention in EU countries mostly due to their suitability to be included in composting processes following their disposal [2].

Among commercially available biodegradable packaging materials based on natural raw materials, those based on starch obtained from cereals, maize, rice or potatoes are the most widely spread [3, 4]. Due to its poor mechanical properties and its hydrophilic nature, starch alone does not form films with adequate mechanical properties (high percentage elongation, tensile and flexural strength) but with mechanical, physical or chemical modifications or in combination with additives become a promising candidate for developing all types of biodegradable packaging materials [5, 6].

Considering its complete biodegradability, low cost and renewability, the large amounts of available raw materials for production and the numerous processing possibilities by extrusion and thermoforming to produce starch-based packaging with a porous structure similar to expanded polystyrene foam (Fig. 1) the starch-biodegradable packaging's have a wide field of applications, successfully replacing the traditional plastics not only in the packaging industry but also in constructions and automotive industry. The properties of starch-based foam packaging depends on the starch type, the contents of blowing agent (water), the content of additive, glycerol and extrusion conditions such as temperature and configuration of the extruder worm [7].

Fig. 1. Structure of corn starch packaging.

The objective of this study was to propose a method for the evaluation of the ultimate biodegradability and degree of disintegration of a corn-starch based packaging material under laboratory conditions simulating an aerobic composting process.

MATERIAL AND METHOD

Principle of test system

By composting, the starch polymeric material is biodegraded by aerobic microorganisms from a compost-inoculum (sludge) suspension, in the presence of oxygen. The inoculum used consists of stabilized matured compost derived from composting the organic fraction of municipal solid waste. The biodegradation of starch based packaging materials was conducted in an experimental installation called "test system" (Figure 2), where temperature, aeration and humidity were closely monitored during the test period. The test system consisted from compressed-air pump (1); flow control device (2); carbon dioxide absorption system made from dry soda-lime or aqueous solution of potassium hydroxide (3); carbon dioxide absorption bottle filled with $Ba(OH)_2$ (4); composting vessel (5); magnetic stirrer with temperature control (6); carbon dioxide trap consisting from two gas bubblers containing alkaline solutions of NaOH and $Ba(OH)_2$ (7); retort stand (8).

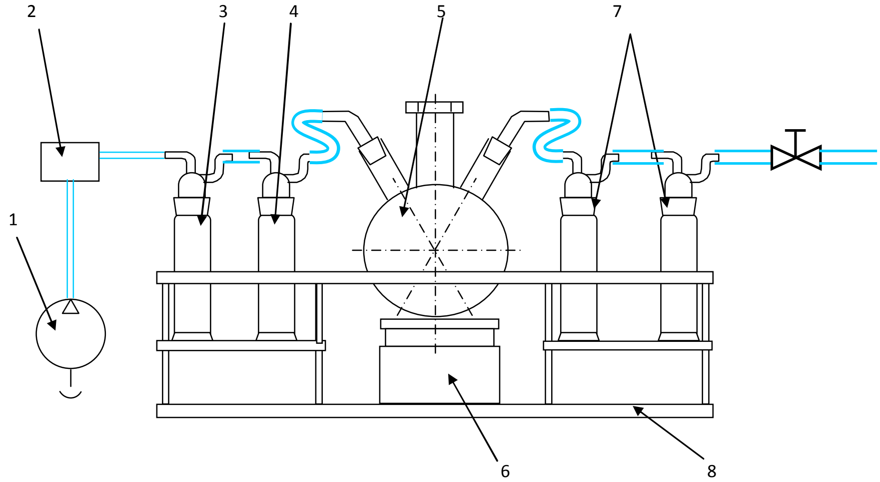

Fig. 2. Layout of the test system

The composting vessels were connected in series through gas-tight tubes, non-permeable to carbon dioxide with the air supply. Carbon dioxide-free air with an optimal high flow rate (50 ~ 100 mL/min) was supplied at a constant low pressure. The air flow rate was checked regularly at each outlet by using wash-bottles to ensure that there are no leaks in any part of the system and using a flow control device. The carbon dioxide was removed by passing the air through a carbon dioxide absorption system (dry soda-lime). CO_2-free air was used to aerate the test mixture in the composting vessel. After biodegradation, the produced carbon dioxide was absorbed in a carbon dioxide trap containing alkaline solutions of 0.05 mol/l NaOH in case of DIC determination and $Ba(OH)_2$ 0.125 mol/l for the titrimetric determination.

During the aerobic degradation of the test material the ultimate biodegradation products: carbon dioxide, water, mineral salts and new microbial cellular constituents (biomass) resulted. The carbon dioxide produced was continuously measured at regular intervals in test and blank vessels in order to determine the cumulative carbon dioxide production.

The used inoculums-compost was a homogenous, well aerated mixture of 2-6 months old farmyard compost containing garden, orchard, food and household waste and activated sludge from a municipal waste water treatment plant.

For the physico-chemical characterization of the inoculum and activated sludge the following parameters were determined: pH, total dry solids content (at 105 ^{o}C), volatile solids (at 550 °C), organic carbon content, nitrogen content and C / N ratio, and ammonium ion [8].

Cellulose with grain size below 20 µm was used as positive control reference material, due to its high percentages of biodegradability (70%) at the end of the test period.

Packaging test material, with dimensions of 20 mm × 20 mm, containing sufficient organic carbon to yield carbon dioxide in an amount suitable for the determination was used. A minimum of 50 g of total dry solids containing 20 g of TOC (total organic carbon) was introduced in each vessel. The C/N ratio for the test mixture was between 10 and 40. The blank vessels contained only inoculum in the same amount of dry solids and volatile solids as the test vessels.

Three composting vessels containing: *i*) inoculum-compost, *ii*) inoculum-compost: cellulose (6:1 ratio), *iii*) inoculum-compost: corn starch-based packaging (6:1 ratio) were incubated for 30 days. During the composting process temperature, humidity, flow rate and stirring were closely monitored and controlled. The carbon dioxide evolved was measured, at 24 hours intervals, after absorption in 0.125 mol/l $Ba(OH)_2$ by tritration of the unreacted $Ba(OH)_2$ with 0.05 mol/l HCl.

Additionally the carbon dioxide evolved of each composting vessel absorbed in 100 ml of sodium hydroxide solution 0.05 mol/L was measured at 5 days as dissolved inorganic carbon (DIC) with a Multi N/C 2100S analyzer usig NDIR detection (Analytic Jena, Germania) [9-14]. The amount of carbon dioxide produced was calculated according to:

$$(CO_2)_T = (DIC_T - DIC_B)\times\frac{3,67}{10} \quad (1)$$

where:

$(CO_2)_T$ – the amount of carbon dioxide evolved, in milligrams; DIC_T –dissolved inorganic carbon, in milligrams; DIC_B - dissolved inorganic carbon measured on the control of NaOH solution, in milligrams, 3.67 - ratio between the molecular weight of CO_2 (44) and atomic mass of carbon (12); 10 - correction factor for a volume of 100 mLof sodium hydroxide solution.

Subsequently it is calculated the theoretical amount of evolved carbon dioxide ($ThCO_2$), in miligrams, according to:

$$ThCO_2 = m \times X_c \times \frac{44}{12} \quad (2)$$

where:

m - is the weight of the test material, in miligrams; X_C is the proportion of total organic carbon in the test material, determined by chemical formula or calculated from elementary analysis, in mass fraction; 44 and 12 - are the molecular mass of carbon dioxide and atomic mass of carbon, respectively.

From the cumulative amounts of carbon dioxide released, calculated the percentage biodegradation, D_T, of the test material for each measurement interval according to:

$$D_T = \frac{\sum(CO_2)_T - \sum(CO_2)_B}{ThCO_2}\times 100 \quad (3)$$

where:

$\sum(CO_2)_T$ is the cumulative amount of carbon dioxide evolved in each composting vessel containing starch, in milligrams per vessel; $\sum(CO_2)_B$ - is the mean cumulative amount of carbon dioxide evolved in the blank vessel, in milligrams per vessel; $ThCO_2$ - is the theoretical amount of carbon dioxide which can be produced by the test material, in milligrams per vessel.

RESULTS AND DISCUSSION

Determination of physico-chemical properties of the inoculum

The physico-chemical parameters of the inoculum were: pH (1:5) 7.71; total dry solids content (at 105 ^{o}C) 50%, volatile solids (at 550 °C) 29%, organic carbon content 33.93%, nitrogen content 8.79 % and ratio C / N 3.86. The physico-chemical parameters for activated sludge were: dry matter 2.481 g/L, volatile matter 48.64 % calcined residue 0.702 g/L and ammonium ion 1.49 mg/L.

The physico-chemical properties of the innoculum and activated sludge from the literature were: total dry solids content between 50% and 55%, the volatile solids content less than 15% of the wet solids or 30% of the dry solids; pH (inoculum:water, 1:5) between 7.0 and 9.0. The inoculum in the blank produce between 50 mg and 150 mg of carbon dioxide per gram of volatile solids over the first 10 days of the test.

After composting of cellulose and packaging materials in each container was produced carbon dioxide that was absorbed in alkaline solutions: barium hydroxide and analyzed every two days and sodium hydroxide in 5 days, during 30 days.

The amount of CO_2 evolved, in mg/L, from each composting vessel, by analytical method (titrimetric), is presented in Table 1 and the biodegradability curve is presented in Figure 3.

Table 1

The amount of CO_2 evolved from biodegradation of compost, packaging and cellulose determined by titrimetric method

Time (days)	CO_2 evolved - compost (mg/l)	CO_2 evolved-packaging (mg/l)	CO_2 evolved-cellulose (mg/l)
2	0	0	0
4	36	60	136
6	54	105	230
8	86	160	297
10	119	235	365
12	132	360	495
14	145	436	521
16	160	470	530
18	173	475	535
20	220	490	539
22	225	500	560
24	235	510	563
26	237	525	570
28	240	530	575
30	241	535	578

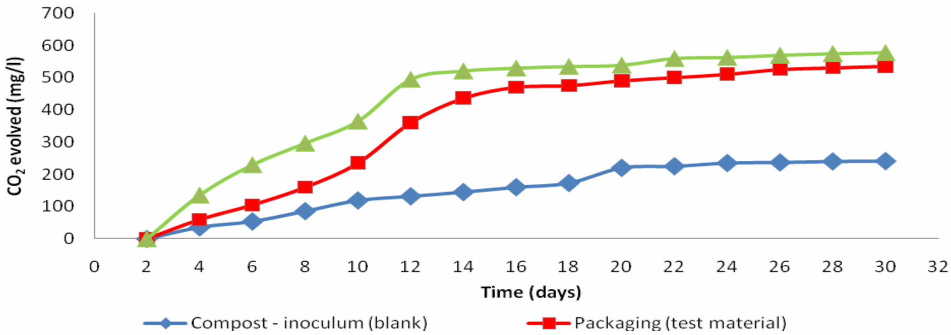

Fig. 3. CO_2 evolution curve by titrimetric method

After 30 days, the cellulose was degraded to the stationary phase at a rate of 63.0% while composted corn starch packaging reached a biodegradation level of 46.5%.

The amount of CO_2 evolved, in g/L, from each composting vessel, determined by the dissolved inorganic carbon method (DIC), is presented in Table 2.

Table 2

The amount of CO_2 evolved from biodegradation of compost, packaging and cellulose determined by dissolved inorganic carbon method

Time (days)	IC (g/L)				D_T (%)	
	NaOH	compost-inoculum	packaging	cellulose	packaging	cellulose
5	0.094	0.081	0.240	0.259	1.18	1.02
10	0.094	0.081	0.253	0.325	1.28	1.70
15	0.094	0.081	0.295	0.349	1.60	1.85
20	0.094	0.081	0.307	0.530	1.69	3.10
25	0.094	0.081	0.324	0.550	1.81	3.45
30	0.094	0.081	0.330	0.555	1.85	3.50

The percentage of biodegradation is given by the ratio between the amount of carbon dioxide produced by packaging material and theoretical maximum amount of carbon dioxide that could be released material. The maximum theoretical produced amount of carbon dioxide is calculated from the measured total organic carbon (TOC). The graphical representation of carbon dioxide evolution is presented in Figure 4.

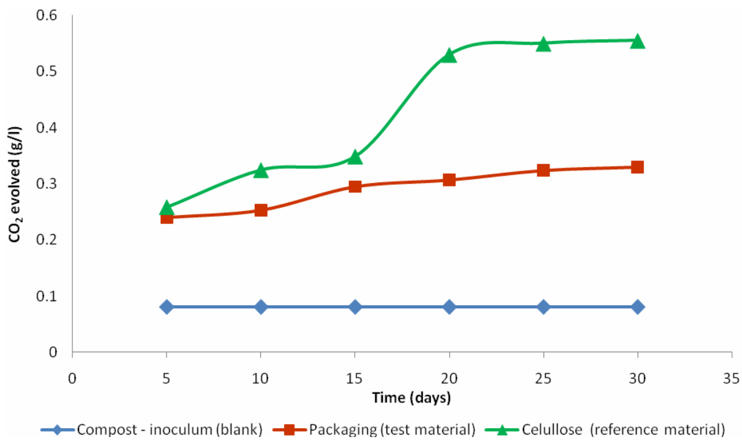

Fig. 4. CO_2 evolution curve by dissolved inorganic carbon method

The percentage biodegradation of cellulose and compost is about 87.7% in 30 days and starch-based packaging is about 56.5%, respectively. The biodegradation rate does not include the amount of carbon converted to new cell biomass.

CONCLUSIONS

A biopolymer packaging material was aerobic composted in an environment where temperature, aeration and humidity are closely monitored and controlled. Better results regarding the percentage biodegradation of corn starch-based packaging during experimentations were obtained by DIC than titrimetric method: approximately 46.5% by titrimetric method and approximately 56.5% by DIC respectivelly.

Biopolymers are derived from renewable resources and therefore produce no net increase in atmospheric carbon dioxide. Biopolymers are biodegradable, unless heavily modified, and can be composted, thus promoting an environment-friendly waste management system. Composting is useful and often preferred method designed to improve soil fertility status by using composted organic wastes.

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