

Study of the Biodisintegration on a Painted Bioplastic Material Waste

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The influence of the painting process on a biocompostable waste is studied. Disintegration degree (D %) of a 100% biocompostable plastic made from potato almidon is calculated for both painted and non-painted samples. Solid matrix is also characterized by means of a laboratory scaled composting process following UNE-EN norms [2, 3]. It can be concluded that painting has a negative influence on biocomposting process decreasing 4.48% disintegration degree. Average D% for painted samples is 84.56 %, and 89.04 for non-painted ones. Regarding to solid matrix, dry mass after composting is double (91.12 %) as before process (43.63 %) for painted samples and 91 % and 45.41 % after and before composting for non-painted samples. Volatile solids are reduced 5.17 % after composting for painted samples, and 8.78 % for non-painted. Organic nitrogen is reduced 0.34 % and 0.16% for painted and non-painted samples respectively. The negative effect of painting is mainly due to the barrier effect of the paint that prevents microorganisms from converting organic components of the biopolymer into water, CO₂ and compost.

Keywords: biodisintegration; composting; painted; bioplastic; waste

The amount of plastic waste is growing every year due to the numerous applications where plastic is used. The management of these wastings can be made by several means such as mechanical and chemical recycling, combustion, landfills or biodegradation. Mechanical recycling is the most extended way of reusing the plastic wastes, but when recycling, mechanical properties and other affecting the plastic processability are modified as described in [12], especially when the number of recycling cycles applied is increased. Besides, most of the recycling is carried out with scrap material from industry and not from household usage. Feedstock recycling covers a range of plastic recovery techniques to make plastics, which break down polymers into their constituent monomers, which in turn can be used again in refineries, or petrochemical and chemical production. Although this kind of recycling is more tolerant to impurities than mechanical recycling; consumption of used material is too high to be viable. Regarding to landfills, their environmental impact is too high to be an environmentally friendly alternative [24]. Taking this panorama into account, development of biopolymers, made from natural sources and easily degradable, arises as the better option for plastic waste management.

The lack of fossil sources and the arising of environmental regulations promote the development of new materials and products more environmental friendly than fossil fuels. In this context, bioplastics fit perfectly to the new industrial and social requirements. Obtaining new materials and chemical products from renewable sources is not a new idea, but the challenge is to develop the required technology and to adapt products and processes to real and competitive applications. However, the applications are carrying the promotion of defining new materials and types of bioplastics. Bioplastics are

classified into two groups: biopolymers coming from renewable source, and biodegradable polymers which agree European biodegradability and compostability regulations [1, 4, 6, 11].

Biopolymers coming from renewable sources include biopolymers whose monomers come from biomass (almidon, cellulose, proteins or lipids), or biopolymers whose monomers are produced by means of fermenting renewable sources although the following polymerization process is a conventional chemical process, such as polylactic acid (PLA), that is one of the most studied biopolymers [8, 9]. Another way of synthesizing biopolymers is by biotechnological procedures such as polyhydroxy-alcanoate (PHA), [23], mainly from microbial fermentation or from technologies based on genetically modified plants [18].

Biodegradable polymers are those that are converted into natural substances such as water, carbon dioxide and compost thanks to the action of microorganisms that are available in environment. Biopolymers are usually biodegradable and compostable although this fact is not necessary to be considered as bioplastic. On the other hand, biodegradable materials do not need to come from renewable sources to agree regulation EN [1] about biodegradation, because biodegradability is more related to chemical structure than to the origin of the raw material.

Benefits of bioplastics can be summarized as follows: first, an increasing of resource efficiency because the resources can be cultivated on a periodical basis as well as the cascade use of the resource, first as material, and then for energy generation; secondly, a reduction of carbon footprint and GHG emissions of some materials and products; thirdly, a saving of fossil resources for substituting them progressively, [7].

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Biocompostable materials are those capable of being decomposed during a composting process under controlled condition of biodegradation without leaving toxic remainders [16, 17]. The classification of a material as biocompostable depends of the determination of its total biodegradability, its disintegration degree, and the possible ecotoxicity of the degraded material, determined according to standard tests [1, 21]. Any fact affecting the reactivity of the biocompostable material has influence on the biopolymer degradation rate [15].

This research work is focused on analyzing the influence of painting on degradation of a biocompostable material made from potato almidon. To analyze this influence biodegradation degree of both, painted and non-painted samples will be calculated at laboratory scale following normative [2,3].

Experimental part

Bioplastic material preparation

The investigated material was a 100% compostable and biodegradable plastic made from potato almidon. Material reference is 100% BIOPLAST GF 106/02 and it is manufactured by SPHERE-SPAIN into shopping bags with a commercial final usage at AENA airports, whose reference is BOLSA ASA LAZO 50/43X60. The bags follow the European normative EN [1]. Size of the bags is 500x430 mm and their thickness is 60 mm.

Two kind of bags were used, water painted with random colors (samples A), and not painted (samples B). Paint used in this research is a water paint referenced as IDROSTAR supplied by CHIMIGRAF. Composition of the paint is 15% solid synthetic resin and pigments, 75% water, 2.5% 1-metoxi-2-propanol, 7.5% ethanol. Water paints are the only allowed by regulations for biopolymers, so dissolvent based paints (25% solid pigments based on toluene, 75% dissolvent based on butan-1-ol) used for conventional polymers are not applicable for this purpose.

To carry out the experiments, these bags were cut into smaller pieces 25x25 mm, and vacuum-dried at $40 \pm 2^\circ\text{C}$ for 72 h. Figures 1 and 2 show bags and samples used.

Methodology

Norms EN 14806, "Packaging. Preliminary evaluation of the disintegration of the packaging materials under simulated composting conditions in a laboratory scale test" [2, 3] "Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test" [3] were followed to evaluate the biodegradation degree of the pieces of bags. These regulations are used because they establish the conditions to evaluate bioplastics biodegradation in a laboratory-scale test as used for this research. According to these regulations, bag samples were mixed with a solid biodegradable synthetic material, provided



Fig. 1. Painted bag delivered by AENA (a); Non painted bag provided by SPHERE-SPAIN with reference BOLSA ASA LAZO 50/43X60 (b)



Fig. 2. Painted bag after having been cut into pieces (a); Non painted bag after having been cut into pieces (b)

by GESTCOMPOST S.L., a full scale aerobic composting plant located in Pina de Ebro (Zaragoza, Spain), and subject to aerobic degradation. The composition of the synthetic material was the following (as percentage of dry mass): 10% compost, 40% wood sawdust, 30% rabbit food, 10% corn starch, 5% sucrosa, 4% corn oil and 1% urea. The commercial compost corresponded to a three months old mature compost and was sieved through a 5 mm sieve before adding to the mixture.

The experiments were carried out by triplicated with samples A (painted A1, A2, and A3), and samples B (non-painted B1, B2, and B3). Also a reactor containing wet synthetic material without plastic pieces was prepared (reactor "Blank").

An amount of 19-20 g of plastic pieces was mixed with 1 kg of wet synthetic material (55 wt% of water according normative), and put into a polypropylene reactor. The polypropylene reactors of 290 mm x 190 mm x 105 mm (length, width, height) were hermetically sealed to avoid excessive evaporation. Anyway it has holes of 5 mm in the middle of the small side of the reactor at 65 mm from the bottom for providing air exchange. Table 1 summarizes the initial weights of synthetic material and the corresponding amounts of plastic added to each reactor.

Table 1
AMOUNTS OF SYNTHETIC PLASTIC PLACED INTO EACH REACTOR

Reactor	Total amount of plastic (g)
A1	19.4013
A2	19.7956
A3	19.8773
B1	19.4672
B2	19.8557
B3	19.5459

An analysis of volatile suspended solids (VSS) and dry mass following Method 2540G of "Standard methods", [5], and C/N relationship was carried out before the experiments to check the synthetic material. C/N relationship was calculated considering that the % of carbon corresponds to VSS value divided by 2[2, 3], whereas the content of nitrogen corresponds to N-Kjeldhal, which was analyzed following Method 4500-N_{org} of "Standard Methods" [5].

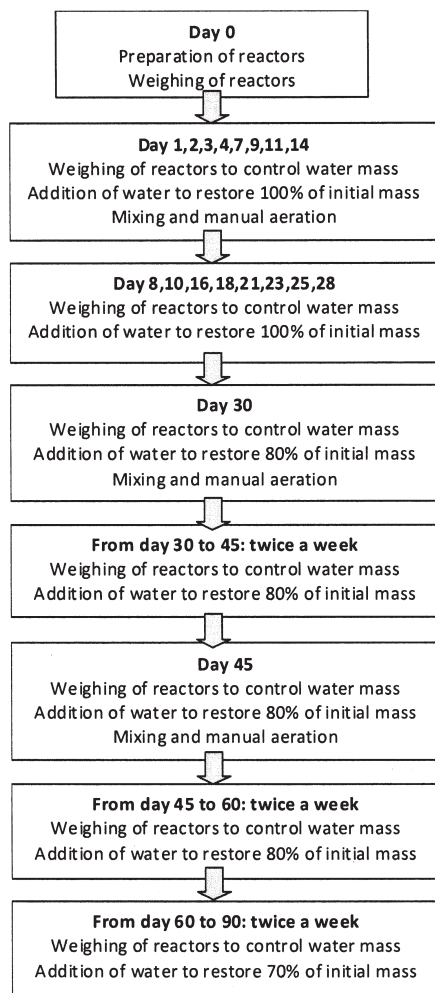


Fig. 3. Task schedule during composting time

The aerobic degradation was carried out in an air circulation oven supplied by Climats-SAPRATIN 505 mm x 490 mm x 305mm, according to [13], at a constant temperature of $58 \pm 2^\circ\text{C}$ for 90 days. Moisture, mixing and aeration of the samples were periodically controlled [14], as recommended by [23]). Also pH, visual aspect, oven temperature and odor were measured in order to analyze its evolution. Procedure during composting time is shown on figure 3.

At the end of the composting period, the composts of each reactor were characterized by means of determining the VSS, moisture and N-Kjeldhal. Each compost was dried at $58 \pm 2^\circ\text{C}$ and sieved with the objective of separating the remaining plastic pieces greater than 2mm. The recovered fragments were washed with distilled water, dried at $40 \pm 2^\circ\text{C}$ until constant mass, and weighed for calculating the corresponding biodisintegration degree

$$D = \left[\frac{M_i - M_f}{M_i} \right] 100 \quad (1)$$

where M_i corresponds to the initial dry mass of plastic material and M_f represents the dry mass of the recovered plastic material after composting and sieving.

Two criteria are considered to validate the composting process. Firstly, the biodisintegration degree (D) for all the samples of the same kind must not differ more than 10%, and secondly the volatile solids decreasing (R) must be $\geq 30\%$.

$$R = \frac{[m_i (DM)_i (VS)_i] - [m_f (DM)_f (VS)_f]}{[m_i (DM)_i (VS)_i]} 100 \quad (2)$$

where m_i denotes the initial mass of the wet synthetic material before composting, $(DM)_i$ is the initial dry mass of synthetic waste (as % of total mass) and $(VS)_i$ represents the volatile solids of the initial synthetic material (as percentage of DM). The term m_f corresponds to the final dry mass of the obtained compost, $(DM)_f$ represents the final dried mass of compost (as % of total mass) and $(VS)_f$ is the volatile solids value of the obtained compost (as % of DM).

Results and discussions

Initial solid synthetic material characterization

As previously stated, some parameters such as dry mass, volatile solids and C/N relationship were previously determined for each reactor in order to verify if the initial synthetic material was adequate for carrying out the composting reaction (table 2). It is observed that the percentage of dry mass was according to normative that recommends 45%. The average content of volatile solids was 90.25%, indicating a high content of organic matter. C/N relationship calculation is not mandatory by regulations and so, only two of the three reactors of each type is calculated. An initial value between 20:1 and 40:1 is recommended and in this case, the C/N average value was 27.89:1, which is considered adequate for composting.

Monitoring and control of the composting experiment

Three parameters must be controlled during the experiments to validate the adequate progress and final results of the tests. The composting reaction was periodically controlled by measuring the temperature as well as determining the pH and content of moisture of each reactor. To validate the composting experiment temperature must remain at temperature reference $\pm 2^\circ\text{C}$, pH must follow the theoretical trend of a real composting

Reactor	Dry mass (%)	Volatile solids (% dry mass)	Carbon (% dry mass)	Nitrogen (% dry mass)	C/N
A1	45.24	91.54	45.77	1.97	23.29
A2	42.21	89.24	44.62	1.88	23.80
A3	43.44	89.03	44.51	n.a.	-
B1	46.63	90.46	45.23	1.43	31.58
B2	45.74	89.94	44.97	1.47	30.50
B3	43.85	89.44	44.72	n.a.	-
Blank	47.09	92.11	46.05	1.52	30.28
Average	44.89	90.25	45.13	1.65	27.89

Table 2
PERCENTAGES OF DRY MASS, VOLATILE SOLIDS, AND C/N RELATIONSHIP OF EACH REACTOR BEFORE COMPOSTING

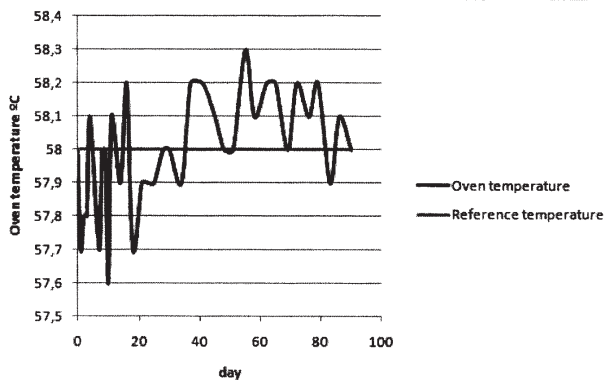


Fig.4. Temperature variation into the oven versus time, during composting period

plant, and content of moisture must follow the theoretical trend as described in table 3.

The temperature was maintained at $58 \pm 2^\circ\text{C}$ as it is shown in figure 3, so room temperature had not any influence on the oven temperature.

Figure 5 shows that pH variations of each reactor over time correspond to the theoretical evolution of a real composting plant [10, 20]. Experimental pH values are similar to those described theoretically by normative. A decreasing of pH at the beginning of the composting period is caused by mineralization of the organic matter. The organic matter of the mixture was converted into carbon dioxide and water. From days 8-10 to day 25 pH increases gradually from acid values (6-6.5) to basic values (8-9), due to the release of ammonia and other basic components in the mixture and the elimination of organic acids according to [22]. From day 25, pH decreases from basic values (8-8.5) up to neutral ones (7-7.5). All the reactors, included blank follow the desired trend described for a real composting plant.

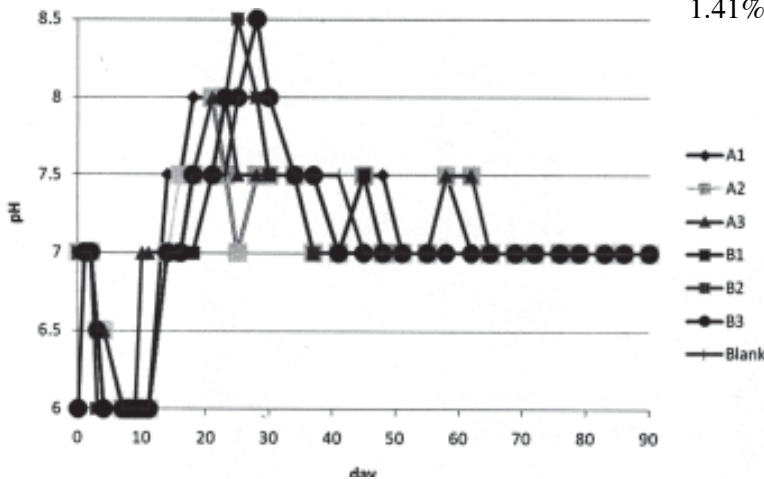


Fig. 5. Ph variation of each reactor during the composting time

To adequate the seven reactors to oven dimensions and accordingly to experience of other experiments [19], an initial layout of three levels was disposed including a clockwise periodical change of the position of the reactors to make sure the proper variation of moisture content, taking into account the importance of water content in microbial activity for composting and rate of degradation.

The uniform variation of moisture content of each reactor after periodical changes is shown in figure 6. As described on it, the initial amount of water of each reactor was 550 g and losses of water were observed in all the reactors during the composting period. Distilled water was added to the reactors in order to maintain the optimal percentage of moisture as the Norms recommend (fig. 3). All the reactors follow the theoretical trend recommended.

Characterization at the end of the composting experiment

After 90 days of composting reaction, each reactor was characterized. Values of final dry mass, volatile solids and nitrogen are shown in table 3. The reduction in volatile solids content of reactors "A" and "B" was within 3-7.8% and 5.68-11.81% respectively. The "Blank" reactor has a reduction of 9.74% which is on the average of the obtained results. It indicates that the pieces of plastic have not a negative influence on the composting reaction. The final content of volatile solids of each compost was slightly lower than before composting, indicating that a part of organic matter is transformed into carbon dioxide. On the other hand, the % average values of organic nitrogen decreased from 1.92 to 1.58% in reactors "A", and from 1.45 to 1.28% in reactors "B". This fact is probably due to nitrogen conversion to ammonium, nitrites and nitrates. The reduction of reactor "Blank" was on the average decreasing from 1.65 to 1.41%.

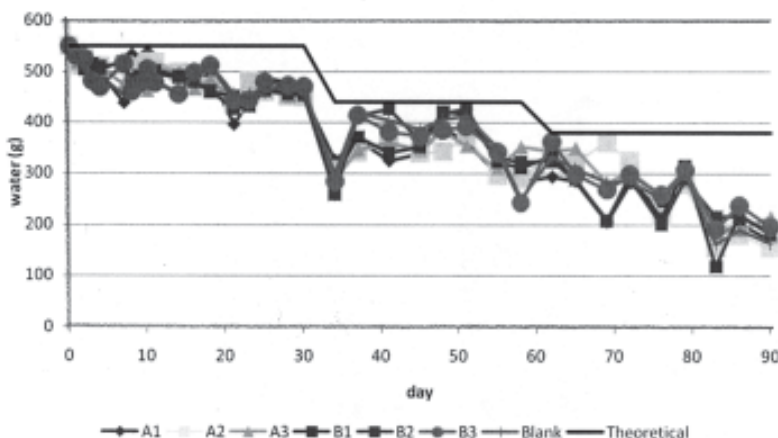


Fig. 6. Variation of the amount of water during composting time

Table 3
PERCENTAGES OF DRY MASS, VOLATILE SOLIDS, AND NITROGEN AT THE END OF COMPOSTING TIME

Reactor	Dry mass (%)	Volatile Solids (% dry mass)	Nitrogen (% dry mass)
A1	91.15	84.34	1.62
A2	91.13	86.54	1.55
A3	91.09	83.42	n.a.
B1	91.87	79.82	1.25
B2	89.75	84.83	1.32
B3	91.39	78.87	n.a.
Blank	89.79	83.13	1.31
Average	90.88	82.99	1.41

n.a: not analyzed

Reactor	m_i (g)	$(DM)_i$ (%)	$(VS)_i$ (%)	m_f (g)	$(DM)_f$ (%)	$(VS)_f$ (%)	R (%)
A1	1011.1	45.24	91.54	307.7	91.15	84.34	43.52
A2	1004.2	42.21	89.24	314.0	91.13	86.54	34.53
A3	998.3	43.44	89.03	303.2	91.09	83.42	40.33
Average "A" samples							39.46
B1	1002.4	46.63	90.46	323.8	91.87	79.82	43.85
B2	1007.7	45.74	89.94	333.1	89.75	84.83	38.83
B3	1000.9	43.85	89.44	315.7	91.39	78.87	42.03
Average "B" samples							41.57
Blank	999.1	47.09	92.11	340.0	89.79	83.13	41.43

Biodisintegration calculation

The exact amounts of plastic pieces before and after composting of each reactor, as well as their corresponding biodisintegration degree (D) calculated according to equation 1 are shown in table 4. It can be observed that, in all cases, more than 50% of the initial plastic material was degraded. The biodisintegration degree of the painted samples ("A samples") had an average value of 84.56%, which is lower than the value obtained for non-painted samples ("B samples"), whose average value is 89.04%. This fact could be explained because although IDROSTAR water paint used has OK Compost Conformity Mark (Vinçotte 2014), disintegration degree for water paints is lower than for the biopolymer itself. In addition, composting process is carried out by microbial organisms converting organic components of the product into water, CO₂ and compost. As paint actuates as barrier preventing these microorganisms from reaching biopolymer components, the microorganisms only can degradate paint organic components with a lower disintegration degree.

Validation of biodisintegration tests

The validation of the results of the biodisintegration experiments of both "A" and "B" samples are carried out by means of calculating, the volatile solids decreasing for each reactor according to equation 2. Table 5 shows the obtained values.

According to Norm ISO [3], the results of R can be considered valid as all the calculated values are greater than 30%. On the other hand, the variability of the

Table 4
AMOUNTS OF PLASTIC MATERIAL BEFORE AND AFTER COMPOSTING AND CALCULATED BIODISINTEGRATION DEGREE (D)

Reactor	Initial mass (g) M_i	Final mass (g) M_f	D (%)
A1	19.4013	3.3345	82.81
A2	19.7956	2.9871	86.91
A3	19.8773	2.7891	85.97
Average "A" samples			84.56
B1	19.4672	2.2132	88.63
B2	19.8557	1.9088	90.39
B3	19.5459	2.3255	88.10
Average "B" samples			89.04

Table 5
VALUES NEEDED FOR CALCULATING THE VOLATILE SOLIDS DECREASING (R) OF EACH REACTOR

biodisintegration degree (D) should be lower than 10%. As it can be seen in table 5, the variability depends on the initial tested material. "A" samples can be considered valid as the obtained values are not divergent (82.81-86.91%). D values for "B" samples are also valid (88.10-90.39%).

Conclusions

It has been found that painted samples present an average biodisintegration degree lower than not painted ones. D values are 84.56% for painted samples and 89.04% for non-painted ones.

Dry mass after composting is reduced from 91.12 % to 43.63 % for painted samples and from 91 to 45.41 % for non-painted samples. Volatile solids are reduced 5.17 % after composting for painted samples, and 8.78 % for non-painted. Organic nitrogen is reduced 0.34 % for painted samples, and 0.16 % for non-painted ones.

As a general conclusion, biomaterials should be also used for painting and decoration of the products manufactured from biopolymers in order to reach the global aim of making easier the degradation of polymer waste.

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Manuscript received: 3.07.2014