

Interaction and Biodegradation of UV/EB Cured Print Inks Applied to a Compostable Polymer Blend

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Abstract

The use of compostable polymers has largely increased in short lifetime product applications, and most of these products contain printed information, which are mostly produced by ultraviolet/electron beam radiation (UV/EB) curable printing inks. However, when compostable polymers are used, they are printed with non-biodegradable UV/EB inks raising a question if the final printed structure is still compostable or not. It is important to understand the impact of these different coatings on the compostable polymeric substrates and their overall impact on the degradation of the whole system. The objective of this project was to assess the compostability of poly(butylene adipate-co-terephthalate) (PBAT)/ thermoplastic starch (TPS) blend films coated with different UV/EB radiation curable inks. This work also explores how the incorporation of degradation-promoting additives affects the chemical changes on the compostable polymer substrates and their effect on the overall quality of the compost used during the biodegradation process. In summary, biodegradation of the polymer substrate was reduced up to 35% as assessed by evolution of CO₂. EB-cured samples presented lower biodegradation rate than the UV-cured samples, reflecting that the compostable substrate was cross-linked by the relatively higher penetration of the ionizing radiation. The incorporation of transition-metal salt based pro-degrading additive caused alterations on the initiation biodegradation step (during the 21 days) for the samples with lower curing degree.

Introduction

The inclusion of green technologies in the portfolios of companies from different manufacturing fields is common practice nowadays. For example, in the last decades, UV/EB cured products have shown exponential growth in applications traditionally dominated by solvent-based coatings, such as overprinted varnish or print inks for plastic or paper packaging. This is attributed to the near zero emission of volatile organic compounds (VOC) during the photo-curing of coatings.

In the same context, a strong tendency is observed on the application of environmentally friendly plastics, such as the biodegradable or compostable polymers, on different fields of applications (Figure 1). In order to be considered compostable, the material has to bypass the following reactions after its disposal: mineralization (biodegradation to carbon dioxide, water and biomass), disintegration into a composting system, and the completion of its biodegradation during the end-use of the compost with no negative impact¹. They can be classified into two groups, depending on the source: from renewable ones, such as polylactide (PLA) and thermoplastic starch (TPS), and from petroleum ones, such as aromatic copolyesters and polyesteramides.

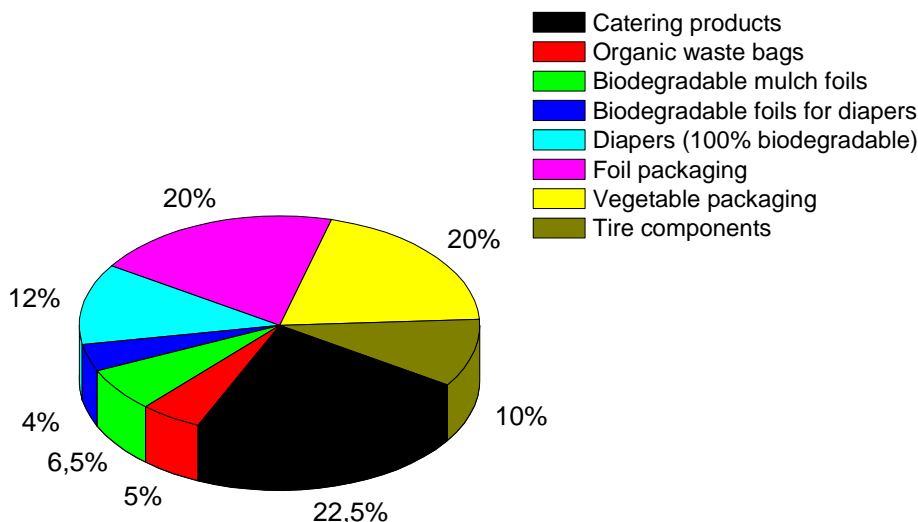


Figure 1. World consumption of biodegradable/compostable polymers by industry. The data were collected in 2012-2013, considering an overall amount of 2 million tons per year².

When UV/EB curable coatings are applied on biodegradable plastic substrates, there is a possibility that the cross-linked ink film will prevent the material from the biodegradation reactions. Additionally, radiation parameters on curing can directly modify the substrate structure, causing undesirable cross-linking or premature degradation. By this way, this project aims to follow and investigate the parameters influencing the biodegradation of coated compostable polymer substrate designed for short lifetime products, and a methodology to increase the rate of consumption of the polymeric systems in a laboratorial composting environment.

Experimental

Substrate: Poly(butylene-co-adipate terephthalate)/thermoplastic starch (PBAT/TPS) blend films were kindly supplied by Corn Products do Brasil (Jundiaí, SP, Brazil), and it was used as the polymeric substrate for printing the ink formulations as specified. PBAT/TPS contained more than 50% renewable polymer (starch). The detailed formulation and production technique are proprietary information. Figure 2 shows the chemical structure for both components of the polymeric blend.

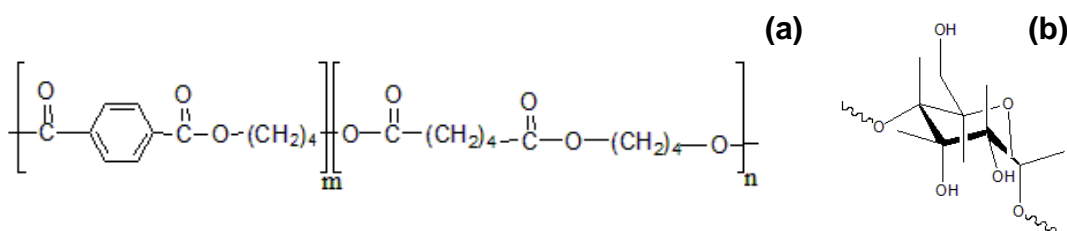


Figure 2. Chemical structure for (a) poly(butylene-co-adipate terephthalate) (PBAT), and (b) starch.

Ink composition: To study the effect of pro-degrading additives on the inks, 1 %wt cobalt stearate (CoSt), supplied by Strem Chemicals Inc. (Newburyport, MA, USA), was added into the ink compositions introduced elsewhere³.

Ink application: A manual applicator type QuickPeek® (Boanitec Indústria e Comércio Ltda., Cotia, SP, Brazil) was used to apply the colored print inks over the PBAT/TPS films. The thickness of the coating layer was $7.0 \pm 1.3 \mu\text{m}$ before curing.

UV curing: The coating formulations were cured at room temperature using a Labcure UV tunnel (Germetec UV and IR Technology Ltd., Rio de Janeiro, RJ, Brazil). Shortly, this equipment consists of a medium-pressure mercury lamp (main photon emission range from 320 nm to 400 nm) and a conveyor belt with adjustable speed. The UV radiation doses were measured with an EIT UV PowerPuck® radiometer from EIT Inc. (Sterling, VA, USA). The coated plastic sheets were put on a conveyor belt able to move under the UV light beam. The power of the lamp was fixed on 11.8 kW m^{-1} , and the precise control of conveyor speed determined the radiation dose absorbed by the samples. So, the UV radiation dose of 5.20 kJ m^{-2} was applied to the samples at 23°C and 45% RH.

UV accelerated aging: The accelerated aging was performed using a QUV chamber model EQUV from Equilam Ind. e Com. Ltda. (Diadema, SP, Brazil) following ASTM D5208-09, cycle C. Fluorescent UV light bulbs with $0.89 \text{ W m}^{-2} \text{ nm}^{-1}$ irradiance (at 340 nm) was used for non-stopping 250 h cycles of irradiation under UV-incident beam at 90° and constant temperature at $50 \pm 3^\circ\text{C}$. After exposition, aged and non-aged samples were characterized and evaluated.

Molecular weight analysis: Each sample of UV-aged PBAT/TPCS blend, control and coated, was dissolved in tetrahydrofuran (THF) at room temperature for seven days and filtered through a $0.2 \mu\text{m}$ polytetrafluoroethylene (PTFE) syringe filter. Molecular weights were measured by a Waters GPC (Milford, MA, USA) equipped with a series of three columns (HR2, HR3, and HR4), and a Waters 2414 refractive index detector interface with Waters Breeze software from Waters Inc. (Milford, MA), using a flow rate of 1.0 mL min^{-1} , an average runtime of 45 min, and a temperature of 35°C . The number-average and weight-average molecular weights, \bar{M}_n and \bar{M}_w respectively, were calculated using a calibration curve obtained from polystyrene standards (Polystyrene Shodex STD KIT SM 105, Showa Denko, Japan) with molecular weight in the range of 1.20 to $3.64 \times 10^3 \text{ g mol}^{-1}$. A third-order polynomial calibration curve was used. The \bar{M}_n and \bar{M}_w of the PBAT part of the blends are reported.

Composting: An in-house built direct measurement respirometric system (DMR) fulfilled by bioreactors connected to a CO_2 infrared gas analyzer was used to determine the biodegradation in organic compost. Three groups of bioreactors were used: the first containing 400 g compost (wet basis) as control sample; the second group composed of a mixture of 400 g compost (wet basis) with 8 g cellulose powder ($20 \mu\text{m}$ grade, Sigma Aldrich, St. Louis, Mo., USA) as positive control; and the third one containing 400 g compost (wet basis) with 8 g of BA-PBAT/TPS, AA-PBAT/TPS, AA-Black, AA-Black-CoSt, AA-Yellow, or AA-Yellow+CoSt films cut into $1 \text{ cm} \times 1 \text{ cm}$ pieces. Each sample was run in triplicate. The test was conducted according to ASTM D5338-11. The bioreactors were incubated in an environmental chamber at $58 \pm 2^\circ\text{C}$ and 55% relative humidity for 60 days. The compost humidity was measured every three days. The CO_2 evolution was continuously monitored. The percent mineralization was calculated using equation (1) where $s\text{CO}_2$ is the amount of CO_2 from the sample or the cellulose reactor; $b\text{CO}_2$ is the amount of CO_2 from the compost reactor; W is the weight of sample or cellulose; and $\%C$ is the % carbon in the film sample or cellulose obtained from elemental analyses

carried out on a Perkin-Elmer 2400 CHN (Waltham, MA, USA). The test met the ASTM D5338-11 requirements by producing 50.8 ± 4.0 mg of CO_2 per gram of volatile solids over the first ten days of the test. The compost had an ash content of less than 70 % and the pH was 7.9 ± 1.0 . The total dry solids were quantified as 52.8%.

$$\% \text{Mineralization} = \frac{scO_2 - bcO_2}{W \times \frac{\%C}{100} \times \frac{44}{12}} \times 100 \quad (1)$$

Ecotoxicity: After the biodegradation test under composting conditions, the content of each replicate vessel was carefully removed and thoroughly mixed. Compost (5 mg) was kept into a moisture analyzer model MX50 (San Jose, CA, USA) at 105°C until a 0.05% weight loss rate was reached, and the weight was recorded as the moisture content. The dry compost was then mixed with distilled water (1:5) and let it rest for 30 min prior to measuring the pH, using an Omega PHB212 pH meter (Stamford, CT, USA). The following tests were conducted in agreement to ASTM D6954-04 and OECD/OCDE 208 (2006). Compost (50 %wt.) containing the original samples exposed to the DMR was mixed with 50% of potting soil (Sure MixTM, Michigan Grower Products, Inc., Galesburg, MI, USA). A mixture of compost used in the DMR experiment with potting soil was used as control. One dicotyledonae and one monocotyledonae specie were used for plant growth tests, *Cucumis sativus* and *Avena sativa*, respectively. Five replicates were done for each test material and control, and five seeds were used per pot. The pots were conditioned at the Michigan State University Greenhouse (Plant Science) at $25 \pm 3^\circ\text{C}$ during the day and $20 \pm 3^\circ\text{C}$ during the night. A photoperiod of 16 h light every 8 h darkness was adopted at a luminance of $350 \pm 50 \mu\text{E m}^{-2} \text{s}^{-1}$, measured at the top of the canopy. The number of emergence, the biomass measurements (shoot dry weight and fresh weight) and the shoot height of the plants as percentage of the controls are reported after 21 days of testing.

Results and Discussion

Figure 3 shows the average values, and the corresponding standard deviation, for carbon dioxide evolution from UV-aged radiation-cured inks applied on PBAT/TPS samples. Table 1 presents the average mineralization values of the evaluated materials calculated in the 21st, 42nd and 58th day of composting.

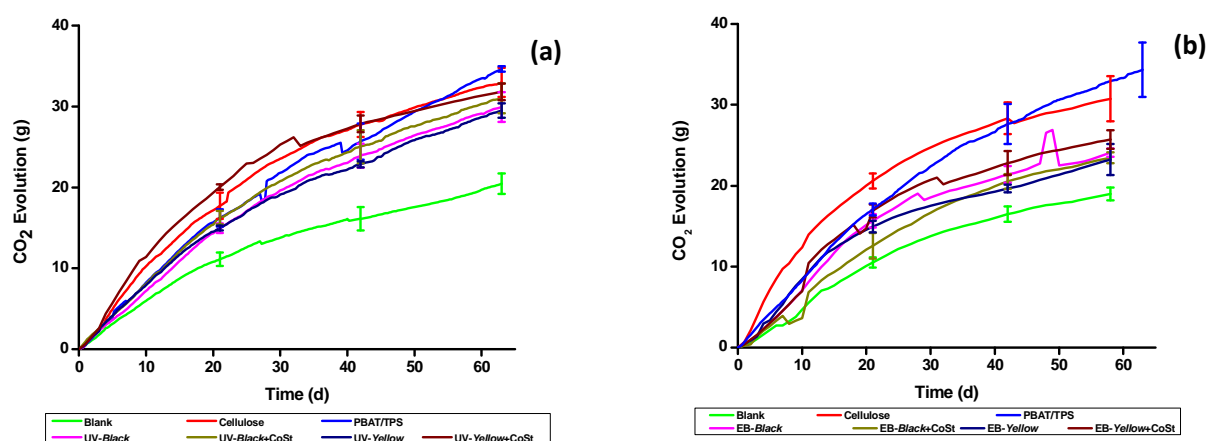


Figure 3. CO₂ evolution for (a) UV-aged UV-cured coated samples, and (b) UV-aged EB-cured coated samples on PBAT/TPS blend film during composting test. Both (a) and (b) contain curves for blank, cellulose and PBAT/TPS blend.

Table 1. Average mineralization values for the test materials on composting environment

Material	Curing Radiation	Mineralization in % after...		
		21 d	42 d	58 d
Cellulose (control)		49.6 ± 13.8	87.7 ± 15.8	96.4 ± 16.3
		78.5 ± 8.7	92.4 ± 17.0	91.8 ± 22.5
PBAT/TPS		37.2 ± 14.6	70.0 ± 28.0	104.0 ± 31.5
Black	UV	24.3 ± 6.9	49.3 ± 13.8	60.4 ± 16.3
	EB	35.5 ± 3.2	34.0 ± 6.1	35.3 ± 4.4
Black+CoSt	UV	31.4 ± 7.3	54.2 ± 15.3	65.0 ± 15.2
	EB	14.2 ± 10.4	28.1 ± 6.6	31.1 ± 5.4
Yellow	UV	28.1 ± 11.7	49.3 ± 20.2	38.4 ± 15.4
	EB	31.2 ± 3.2	22.5 ± 6.6	30.1 ± 11.2
Yellow+CoSt	UV	54.7 ± 7.7	64.5 ± 12.7	67.6 ± 6.3
	EB	45.0 ± 2.7	44.5 ± 6.4	47.5 ± 5.3

It is possible to observe that all the tested samples have produced more carbon dioxide than the blank (Figure 3). This implies that the materials are to be bio-assimilated by the microorganisms in the organic compost with no inhibition to medium. The substrate has shown to be totally compostable. The final mineralization for the PBAT/TPS blend surpassed the mineralization for the positive control cellulose.

When the coating layer is added to the substrate, there is a reduction on the evolution of the carbon dioxide over the time. This is observed for all the studied compositions, independent of the pigment or the radiation curing. In some manner, the cross-linked coating has protected the surface of substrate film against the action of the microorganisms that would act as reducers of the molecular weight. By now, the surface area was half reduced due to the coating layer.

Figure 3 also shows that the samples cured by EB radiation had even less biodegradation reactions taking place on the structure than the ones UV-cured. The relatively high dose rate attributed to the first radiation source will impart a highly cross-linked structure, with higher degree of curing. It is known that the increasing on the cross-linking density increases the degree of protection to film. By another side, the electronic nature of the EB radiation has more depth penetration than the one from ultraviolet photons. This energy is capable to reach the film substrate and then causing cross-linking between the polymeric chains. So, both effects are expected to reduce the mineralization of the EB-cured samples when compared to the UV-cured samples.

Additionally, we can see that different scattering/absorbing properties of the pigments do not significantly interfere on the kinetics of biodegradation. However, the addition of pro-degrading additive has helped to improve the mineralization of compositions containing yellow pigment. This can be attributed to the interference during the curing or aging process: carbon black tends to absorb much more photons and then delivering less energy to the pro-degrading molecules. Cobalt stearate is the element that catalyze the degradation chain reactions on the ink layer; by this way, the substrate is more susceptible to posterior biodegradation steps.

In order to corroborate our discussion, Figure 4 shows the variation in \bar{M}_n and \bar{M}_w of the PBAT part of the blends in function of the curing process, UV-aging and composting. The values for the substrate PBAT/TPS are shown as comparative parameters only.

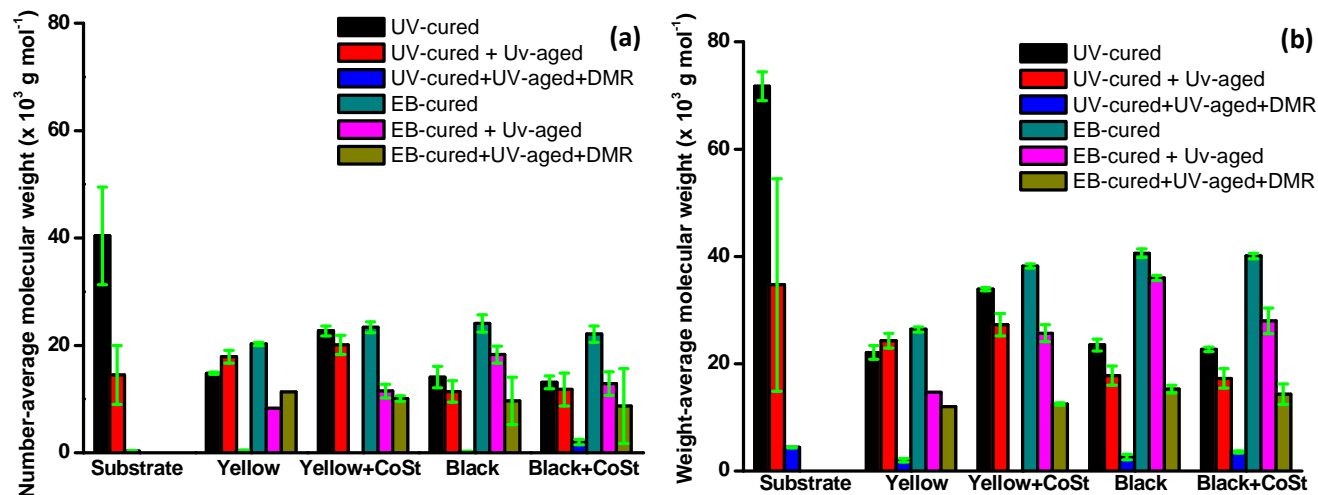


Figure 4. Average \bar{M}_n (a) and \bar{M}_w (b) of the PBAT part of the blend after UV- or EB-curing, UV aging and composting. Substrate PBAT/TPS is shown for comparison-basis only.

The molecular weight is a measurement of the distribution of the polymeric chain fragments on the polymer. The number-average molecular weight (\bar{M}_n) is associated to the distribution by number of molecules, whereas the weight-average molecular weight (\bar{M}_w) represents the distribution of weight. By Figure 4, we observe significantly reduction on the molecular weight for the uncoated substrate, reflecting the effective oxidation and biodegradation processes caused by the UV-aging and composting treatments.

The cured materials, either by UV- or EB-radiation, had a considerable reduction for both \bar{M}_n and \bar{M}_w of the PBAT part of the blends, corroborating with our previous discussion related to the cross-linking of the substrate due to the curing process. Both black and yellow pigmented inks had similar effect on average values for the molecular weight of PBAT. However after composting, the UV-cured yellow-pigmented samples reached the lowest values for molecular weight when compared to the other studied samples. This results corroborate that the interaction of radiation with the pigment particles interferes on the degree of curing and then on the cross-linking density of coating layer, reducing the amount of radiation to reach the substrate.

Tables 3 and 4 present the ecotoxicity of the compost after the composting test of the studied samples by plant growth examination of two different plant species. It is compared UV- and EB-cured coated samples, and blank (control), cellulose (positive control) and uncoated substrate only.

Table 2. Ecotoxicity evaluation for the studied samples in organic compost after composting test using *Avena sativa* seeds

	Curing radiation	<i>Avena sativa</i>				
		Total germinated seeds (%)	Germinated seeds relatively to the control (%)	Height (cm)	Wet weight (g)	Dry weight (g)
Blank (control)		75.0 ± 0.0	-	10.0 ± 1.1	0.1 ± 0.1	0.0 ± 0.0
		80.0 ± 0.0	-	23.4 ± 1.5	2.0 ± 0.2	0.3 ± 0.0
Cellulose		100.0 ± 0.0	133.3	17.3 ± 0.7	1.5 ± 0.3	0.2 ± 0.0
		90.0 ± 11.5	112.5	21.5 ± 1.1	3.7 ± 0.2	0.4 ± 0.1
PBAT/TPS		108.3 ± 14.4	144.4	6.8 ± 0.3	0.1 ± 0.0	0.1 ± 0.0
Yellow	UV	100.0 ± 0.0	133.3	18.2 ± 2.1	0.8 ± 0.1	0.1 ± 0.0
	EB	100.0 ± 0.0	125.0	21.8 ± 1.2	1.3 ± 0.2	0.2 ± 0.0
Yellow+CoSt	UV	60.0 ± 0.0	75.0	21.5 ± 1.1	2.6 ± 0.3	0.8 ± 0.1
	EB	100.0 ± 0.0	125.0	28.0 ± 1.3	2.3 ± 0.0	0.2 ± 0.0

Table 3. Ecotoxicity evaluation for the studied samples in organic compost after composting test using *Cucumis sativus* seeds

	Curing radiation	<i>Cucumis sativus</i>				
		Total germinated seeds (%)	Germinated seeds relatively to the control (%)	Height (cm)	Wet weight (g)	Dry weight (g)
Blank (control)		100.0 ± 0.0	-	3.8 ± 0.2	2.5 ± 0.4	0.5 ± 0.1
		100.0 ± 0.0	-	6.8 ± 0.3	15.2 ± 1.4	1.3 ± 0.1
Cellulose		100.0 ± 0.0	100.0	4.2 ± 0.4	3.9 ± 0.3	0.7 ± 0.0
		100.0 ± 0.0	100.0	7.0 ± 0.2	16.4 ± 0.2	1.6 ± 0.1
PBAT/TPS		100.0 ± 0.0	100.0	4.2 ± 0.2	3.4 ± 0.2	0.6 ± 0.0
Yellow	UV	75.0 ± 0.0	75.0	4.2 ± 0.3	3.9 ± 0.4	0.7 ± 0.0
	EB	100.0 ± 0.0	100.0	6.4 ± 0.3	13.0 ± 1.0	1.1 ± 0.0
Yellow+CoSt	UV	100.0 ± 0.0	100.0	7.8 ± 0.3	12.7 ± 0.8	2.5 ± 0.2
	EB	100.0 ± 0.0	100.0	7.4 ± 0.2	16.6 ± 0.9	1.7 ± 0.1

Regarding Tables 2 and 3, it is possible to observe no toxic effect due to the studied samples biodegradation on the organic compost when compared to both blank and cellulose. Interestingly, the incorporation of CoSt in the ink compositions, independently of the pigment or radiation source, has increased the weight of the plants. According to the literature, traces of cobalt can improve the quality of the plant by increasing the water uptake.

Conclusion

The composting of PBAT/TPS blend is shown to happen under simulated conditions, but it is largely reduced when a radiation-cured ink layer is applied to it. Electron beam-cured samples had even lower degradation kinetics than ultraviolet-cured ones, reflecting both the higher cross-linking density of the coating and some degree of cross-linking of the substrate. The presence of a pro-degrading additive has helped to catalyse the biodegradation of those samples with lower curing degree – the yellow pigmented ones. Regarding the possible ecotoxic effects, this additive has increased the absorption of water and so improving the quality of the plants after the tested period.

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