



# Assessment of UV exposure and aerobic biodegradation of poly(butylene adipate-co-terephthalate)/starch blend films coated with radiation-curable print inks containing degradation-promoting additives



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## ABSTRACT

Biodegradable poly(butylene adipate-co-terephthalate) (PBAT) and thermoplastic starch (TPS) blend films were printed with white, yellow, red, blue, and black inks based on epoxy acrylate resin. Clear PBAT/TPS films were used as the control. Ink formulations were also modified with (1% w/w) and without the degradation-promoting additives cobalt stearate (CoSt) or cerium stearate (CeSt). Printed PBAT/TPS films were cured under ultraviolet light emitted by a medium-pressure mercury lamp at  $10.3 \text{ kW m}^{-2}$ , and then further aged in an accelerated weathering chamber at a total irradiance of  $0.89 \text{ W m}^{-2}$  continuously for 250 h at  $50 \pm 3^\circ\text{C}$ . Subsequently, samples were exposed to an aerobic composting biodegradation process at  $58^\circ\text{C}$  and 55% relative humidity for 60 d. Color ( $L^*$ ,  $a^*$  and  $b^*$ ), gloss and hardness indexes, as well as FTIR spectra, were obtained. Thermal properties and molecular structure were monitored before and after UV exposure and biodegradation tests. The addition of CoSt affected the color, gloss and hardness of the samples exposed to UV aging. The degradation of the PBAT/TPS + CoSt films depended on the nature of the ink pigment and on their capacity to absorb UV photons. UV exposure of PBAT/TPS samples resulted in a larger reduction of weight average molecular weight ( $\bar{M}_w$ ) and the evolution of  $\text{CO}_2$ . The incorporation of the degradation-promoting additives increased the sensitivity of the films to UV degradation, and CoSt had a large impact in the final  $\bar{M}_w$  of the samples.

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## 1. Introduction

The large consumption and waste of short lifetime plastics have increased the environmental concerns raised by both consumers and governments over the last 5 decades (Al-Salem et al., 2009; Hopewell et al., 2009; Kijchavengkul and Auras, 2008; Thompson et al., 2009). One of the main concerns is centered on the difficulty of recycling and/or recovering contaminated plastics, which mostly end up in landfills. Hence, biotic degradation of polymers has been suggested as a tentative method for reducing polymer

waste at end of life (EoL). However, the most commonly used polymers, namely the polyolefins including low, high and linear low density polyethylene (LDPE, HDPE, LLDPE) and polypropylene (PP), and poly(ethylene terephthalate) (PET) (Al-Salem et al., 2009), are largely not susceptible to biological degradation (Kijchavengkul and Auras, 2008). The collection rate of these polymers in many developing and developed countries is very low, and so they accumulate in the environment contaminating vital natural resources, including terrestrial, freshwater and marine habitats (Thompson et al., 2009).

Polyolefins and PET alternatives have been researched in an effort to replace them with biodegradable and compostable polymers. These new classes of materials can be divided into polymers derived from renewable resources, such as starch-based or cellulose-based materials, or non-renewable resources derived from petroleum, such as poly( $\epsilon$ -caprolactone) (PCL) or poly(butylene adipate-co-terephthalate) (PBAT) (Fig. 1a) (Kijchavengkul and Auras, 2008; Thompson et al., 2009). These new

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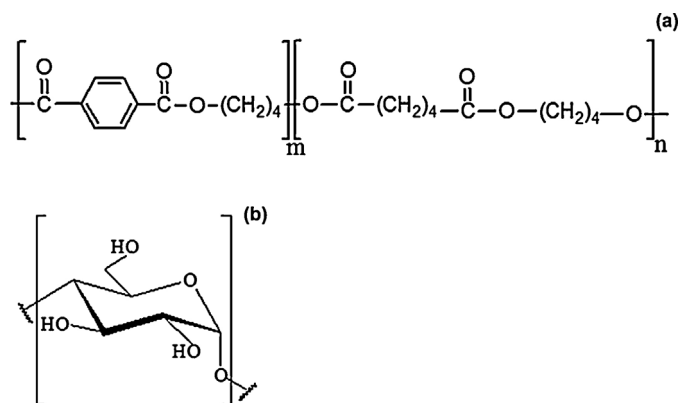


Fig. 1. Chemical structure for (a) poly(butylene adipate-co-terephthalate) (PBAT), and (b) starch.

polymers are easily biodegraded and bioassimilated when disposed on sites containing microorganisms capable of metabolizing their basic chemical structures (Kijchavengkul and Auras, 2008). However, in many cases these biodegradable homopolymers do not meet the physical, mechanical and thermal properties needed for industrial applications. Polymer blends, such as PBAT (Fig. 1a) and thermoplastic starch (TPS) (Fig. 1b) blends, are being developed to meet these requirements (Ojeda, 2013). To be certified as compostable, in accordance with ASTM D6400 and EN 13452, polymers must meet specific disintegration, biodegradation and ecotoxicity requirements (Briassoulis et al., 2010).

In recent years, catalytic agents have been incorporated in polymers to enhance their response to abiotic factors such as levels of UV light exposure, oxygen and temperature (Hopewell et al., 2009). The overall intention of this practice is to reduce the weight average molecular number ( $\bar{M}_n$ ) of the polymers before exposure to biotic environments so that microorganisms can easily digest lower  $\bar{M}_n$  fragments. These degradation-promoting additives are generally called pro-degrading agents, and are mainly transition metal salts. The kinetic reaction mechanism for polyolefin with such additives has been reported (Ojeda, 2013), but it is not yet completely understood for other polymers. On the another side, little is known about the timescale, extent or consequences of their degradation in natural environments (Thompson et al., 2009). ASTM D6954-04 provides some recommendations for testing polyolefin.

Ink layers applied over short lifetime plastic packaging, at around 1–10  $\mu\text{m}$  in thickness after the drying/curing process, have various functions: making the product more attractive to the consumer, supplying information about the product contents, and also offering protection against physical and chemical agents. Inks are basically composed of a resin matrix, diluents, pigments, additives and a curing agent. For this kind of coating, there has been a significant increase in the application of curing induced by UV light or electron beam radiation, also called UV/EB technology. In this technology, the diluent is replaced by reactive monomers, and the formulation is converted into a high cross-linked coating film by means of free radicals generated by the incident radiation. Specifically to the UV curing process, a photoinitiator component is needed (Roy et al., 2010). Once the solid film is obtained, the cross-linked network cannot be easily undone, offering considerably high chemical and physical resistance and stability (Roy et al., 2010).

Thus, the goal of this work was to study the influence of different color inks printed on PBAT/TPS films, cured by UV-B light, and exposed to UV-A degradation followed by an aerobic biodegradation process. The effect of adding a pro-degrading additive into the ink formulation was evaluated for films exposed to UV-aging treatment and biodegradation tests.

## 2. Materials and methods

### 2.1. Materials

PBAT/TPS blend films were kindly supplied by Corn Products do Brasil (Jundiá, SP, Brazil), and it was used as the polymeric substrate for printing the ink formulations as specified. PBAT/TPS contained no more than 50% renewable polymer (starch). The detailed formulation and production techniques are proprietary information.

The following materials were applied in preparation of the UV-curable clear formulation: Bisphenol A epoxy diacrylate (EBECRYL<sup>®</sup> 3720-TP25, Cytec Industries Inc.) diluted 25% by weight with tripropylene glycol diacrylate (TRPGDA, Cytec Industries Inc.); trimethylolpropane triacrylate (TMPTA, Cytec Industries Inc.); a 4.5/3.5/2.0 (w/w/w) blend of photoinitiators (1-hydroxycyclohexyl phenyl ketone (Irgacure 184, Ciba-Geigy Co.)/2-hydroxy-2-methyl-1-[4-(1-methylvinyl) phenyl] propanone (Esacure KIP 150, Lamberti Co.)/2-dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one (Irgacure 379, Ciba Specialty Chemicals Inc.), respectively; talc (Nicon<sup>®</sup> 674, Luzenac America, Inc.); polydimethylsiloxane (Pure Silicone Fluid 100,000cSt, Clearco Products Co., Inc.); quinone derivative in propoxylated glycerol tri-acrylate (Irgastab<sup>®</sup> UV 22, Ciba Specialty Chemicals Inc.); and polyethylene/polytetrafluoroethylene wax (CeraSPERSE<sup>®</sup> 164, Shamrock Technology, Inc.).

Pigments were added to the clear coating to obtain colored print inks as follows: carbon black (Printex<sup>®</sup> 45 powder, Evonik Degussa GmbH); yellow pigment derived from diarylide m-xylidide (Irgalite<sup>®</sup> Yellow LB1W, Ciba Specialty Chemicals Inc.); blue pigment derived from phtalocyanine (Hostaperm Blue B2G 01-BR, Clariant Pigmentos e Aditivos Ltda.); ruby pigment derived from monoazo (Rubide 4B, Hongyan Pigment Chemical Co., Ltd.); and titanium dioxide (Kemira<sup>®</sup> 660 RDI-S, Kemira Pigments Oy). The ratio of pigment/clear coating for the yellow, ruby and blue pigments was kept constant (21/79, w/w) to investigate only the influence of each pigment under UV curing and UV aging. Table 1 provides the nominal composition of the tested samples.

To study the effect of pro-degrading additives on the inks, 1 wt% cobalt stearate (CoSt) or 1 wt% cerium stearate (CeSt), both supplied by Strem Chemicals Inc. (Newburyport, MA, USA), was added to the ink formulation.

The samples were labeled as follows: [BA,AA]-color {+CoSt, +CeSt}. In this format BA and AA stand for “Before UV Aging” and “After UV Aging,” respectively; color is the visual color as presented in Table 1; and +CoSt or +CeSt indicates the presence of cobalt stearate or cerium stearate, respectively. For example, the sample labeled as BA-Yellow + CoSt refers to the PBAT/TPS film coated with yellow ink containing CoSt before UV aging.

## 3. Methods

### 3.1. Ink layer application and curing

A manual applicator type QuickPeek<sup>®</sup> (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.

The coating formulations were cured at room temperature using a Labcure UV tunnel (Germetec UV and IR Technology Ltd., Rio de Janeiro, RJ, Brazil). Briefly, 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<sup>®</sup> radiometer (EIT Inc., Sterling, VA, USA).

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