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# Structural, mechanical and barrier properties of active PLA–antioxidant films

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ABSTRACT

Ascorbyl palmitate (AP) and α-tocopherol (AT) were added to poly-(lactic acid) (PLA) film to investigate their effects on PLA's physical, structural, mechanical and barrier properties. AP crystals appeared on the PLA surface after solvent evaporation and changed PLA transparency. AP decreased the PLA contact angle on the recto side and increased film polarity and wettability. X-ray photoelectron spectroscopy showed that AT increased the concentration of C–(C,H), O=C and O–H bonds on the verso side, but decreased the concentration of C–O and O–C=O bonds. Atomic force microscopy confirmed that the PLA surface microstructure was drastically influenced by the addition of antioxidants in terms of roughness parameters ($R_a$ and $R_q$). AT significantly decreased the film crystallization temperature down to 74.1 °C due to its plasticizing effect. Both AT and AP reduced PLA Young's modulus and tensile strength. PLA water vapor permeability was not significantly influenced by AP and AT. AP is not recommended to be used in PLA active packaging.



## 1. Introduction

Free radicals have been found to be responsible for lipid oxidation, and hundreds of natural and synthetic compounds have been evaluated for their efficiency as radical scavengers or for their other inhibitory effects. Among synthetic antioxidants, only four are widely used in foods, namely butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), and tert-butylhydroquinone (TBHQ) (Wanasundara and Shahidi, 2005). Recently, however, consumer demand for more natural and functional foods has increased because of their positive health benefits and the potential negative health effects of synthetic antioxidants.

The tocopherols are mainly present in oilseeds, oils, meats and the green parts of higher plants, whereas the tocotrienols are mostly found in the germ and bran fraction of certain seeds and cereals. The most abundant natural antioxidants in vegetable oils are the α- and γ-tocopherols, and the most important commercial compounds are α-, γ- and mixed tocopherols. The first two are commonly synthesized, while the latter is a by-product of vegetable oil processing. The antioxidant effects of tocopherols and tocotrienols are due to their ability to donate their phenolic hydrogen to lipid free radicals and retard the autocatalytic lipid peroxidation processes. Alpha-tocopherol (AT) has the highest in vivo antioxidant activity for higher animals and humans, but the efficiency of tocopherols differs in different oxidation conditions (Seppanen et al., 2010).

Ascorbyl palmitate (AP) is a fat-soluble ester of palmitic acid and ascorbic acid, and could be used in oils or fatty foods. AP is a substance that is generally recognized as safe with no specific limitations or restrictions. Ingestion of this antioxidant would pose no health hazards because metabolic breakdown yields ascorbic acid and palmitic acid, both normal metabolites; furthermore it has been shown to be able to regenerate other antioxidants such as tocopherols (Lee et al., 1999; Karabulut, 2010).

Recently, the modification effects of natural antioxidants on polymers, especially biopolymers, have been investigated. Han and Krochta (2007) studied oxygen permeability parameters including the oxygen solubility and diffusivity of two differently-made whey protein isolate (WPI) coatings (powder blended and ethanol solvent mixing) containing 10% of AT and AP. They showed that AP and AT addition increased the oxygen diffusivity approximately 10-fold, and oxygen solubility decreased 10-fold. As a result, the permeability of antioxidant-incorporated films was not enhanced compared to control WPI films. Lopez-Rubio and Lagaron (2010) described the UV stability and mechanical properties of biopolyesters such as poly-(lactic acid) (PLA), polycaprolac-

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ton (PCL) and polyhydroxybutyrate-co-valerate (PHBV) containing β-carotene. They showed a plasticizing effect of β-carotene resulting in a significant increase in the deformation at break and lower Young's modulus. The results confirmed that even though UV radiation degraded β-carotene in polyesters, their mechanical properties remained more stable than those of the pure polymers. The authors therefore suggested β-carotene as a natural additive to increase the UV stability of biopolyesters.

Characterization of extruded PLA-AT was accomplished by Byun et al. (2010). They used polypropylene glycol and BHT as a plasticizer and an antioxidant for film extrusion processing, respectively. They concluded that adding AT to PLA increases its antioxidant activity, oxygen permeability and elongation at break, but decreases film water permeability. According to the authors' conclusion, PLA clarity, which was 20 times less than in pure PLA, is the sole limitation of AT application for PLA active packaging; they did not consider the increase in oxygen permeability as a negative factor for PLA-AT. Gonçalves et al. (2011) studied the addition effect of 2.2% and 4.4% of AT on PLA mechanical, thermal and gas barrier properties. They found no significant changes in the mechanical and thermal properties, but concluded that AT addition increases the oxygen sorption to PLA film.

PLA has been adopted as a biodegradable thermoplastic polyester in packaging, construction, automotive, appliance and medical applications. However, its weaknesses include poor gas-barrier properties, low toughness and ductility, poor thermal stability and high cost, so that many research studies have focused on overcoming these limitations by different polymer modifying methods (Dorgan et al., 2000; Harada et al., 2007). Modifiers such as citrate esters, triacetine, tributyl citrate, oligomeric malonate esteramides, 4,4-methylene diphenyl diisocyanate, polyglycerol esters, polyethylene glycol, acetyl triethyl citrate, talc, bifunctional cyclic ester, and poly (1,3-butylene adipate) have been investigated for PLA improvement (Jamshidian et al., 2010).

Apart from the potential modifying effects of antioxidants, antioxidant-active packaging is an important category of active packaging and a promising technique for extending food shelf-life. Several polymer films have been impregnated with different antioxidants, and the antioxidants' migrations in real foods and food stimulants have been studied (Schwope et al., 1987; Wessling et al., 1999, 2001; Granda-Restrepo et al., 2009). In most studies, the important objectives were the rates, effects and mechanisms of antioxidant release.

Polymer's mechanical, physicochemical and barrier characteristics affect its technical properties and stability in various conditions, whereas its structural properties can influence the rate and amount at which active agents migrate. The first group of characteristics is routinely examined when using modifying compounds, but the structural properties are rarely studied precisely. The addition of active compounds may affect the structure and other physical and mechanical characteristics important to the technological and functional aspects of packaging materials, so an active packaging without the desired properties will be useless. However, the authors believe that the first step in creating a successful active packaging is to identify the effects and interactions between the active compound and the polymer structure. The active agent may have some potential negative effects on the film's functional characteristics; for example, it may cause higher oxygen and water vapor transfer, or weaken the film's mechanical properties.

Atomic force microscopy (AFM) technique can provide precise information about morphological changes made by modifiers that can affect their release into foodstuffs (Kikkawa et al., 2004; Sanchez-Garcia et al., 2008). Surface energy and contact angle provide information concerning the wettability and polarity of the polymer. X-ray photoelectron spectroscopy (XPS) determines the chemical composition of the surface layer and characterizes possible chemical bonding between the modifying agent and the polymer (Kiss et al., 2002).

In this study, the addition effects of two antioxidants, AT and AP, on PLA film made by the solvent-casting method were investigated. The addition of these active compounds may affect the physical, structural, barrier and mechanical properties of PLA film, which are important in respect of the technological and functional aspects of packaging materials. The changes in the thermal and mechanical properties of the obtained materials were addressed using differential scanning calorimetry (DSC) and universal testing machine, respectively. The microstructural surface characterizations of PLA film were analyzed by contact angle, surface energy, XPS and AFM.

## 2. Materials and methods

### 2.1. Materials

Poly-(lactic acid) (PLA), 2002D, was purchased in pellet form from Natureworks® Co., Minnetonka (USA); (+)-α-tocopherol obtained from vegetable oil (1000 $IUg^{-1}$), ascorbyl palmitate (6-O-Palmitoyl-L-ascorbic acid), magnesium nitrate and phosphorus pentoxide from Sigma–Aldrich (France); deuterated chloroform (99.8% $CDCL_3$) from Euriso-Top (France), HPLC-grade chloroform and potassium nitrate from VWR international (France).

### 2.2. Film preparation method

At first a solution of 3.5% w/w of PLA was prepared in chloroform, and afterwards 1% w/w of AP and 2% w/w of AT (2% was used because of supposed higher sensibility of AT to light and temperature) based on PLA dry matter were added to the solution and mixed for 1 h at ambient temperature for complete distribution of antioxidants in the polymer matrix. Because AP was not completely soluble in chloroform, some droplets of pure ethanol were added. Then 20 g of polymer solution was cast in Teflon 90 × 110 mm Petri dishes (Welch, USA). and the extra chloroform was allowed to evaporate in a hood in a dark place over seven days at 25 °C. The Petri dishes were kept in a hermetic container containing $P_2O_5$ powder until the time of each analysis. The final film thickness was 100 ± 5 μm measured (at least eight points) by a mechanical micrometer (Messmer, UK) according to ASTM D 374-99.

### 2.3. Determination of α-tocopherol and ascorbyl palmitate in PLA films

The amounts of antioxidants in PLA films after drying were measured by nuclear magnetic resonance spectroscopy (NMR). $^1H$ NMR chemical shifts in ppm were collected at 600.13 MHz on an Avance III 600 spectrometer (Bruker, Germany) at 298°K. PLA films were dissolved in deuterated chloroform and antioxidants were quantified by comparing the phenolic group peak area of each antioxidant in the sample with phenolic peak area of pure antioxidant solutions (1, 5 and 10 mM). Standard precautions regarding quantization in NMR were taken, including identical spectrometer settings and long enough repetition time between two consecutive scans in comparison with relaxation times. All tests were accomplished in triplicate.

### 2.4. Surface characterization

#### 2.4.1. Film morphological structure

PLA film surface structures were observed at ambient temperature using an Olympus (Provis AX70, Japan) polarizing optical microscope equipped with a digital video camera system.