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Effects of synthetic phenolic antioxidants on physical, structural, mechanical and barrier properties of poly lactic acid film

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ABSTRACT

Synthetic phenolic antioxidants (SPAs) including BHA, BHT, PG and TBHQ were added (1%, w/w) to a poly (lactic acid) (PLA) film. SPA addition had no significant effect on the glass transition and melting temperatures of the PLA film but reduced the crystallinity about 26% and the crystallization temperature by 6–12 °C from the value of 107 °C found for pure PLA film. Young's modulus of PLA film was reduced about 12% by BHA and about 17% by PG and TBHQ. The tensile strength of PLA film also was influenced by BHA, PG and TBHQ. Water vapor permeability of PLA film was not changed by addition of SPAs and PLA oxygen permeability only increased by 30% on BHT addition. No significant changes were observed for surface energy and surface hydrophilicity of PLA films. PLA film microstructures investigated by Atomic force microscopy were significantly changed in term of roughness parameters (R_a and R_q). The results showed that the addition of SPAs in PLA for the creation of active packaging had no negative effect on PLA technical properties.

1. Introduction

Poly (lactic acid) (PLA) is a highly versatile, biodegradable, aliphatic polyester made from 100% renewable resources, such as corn and sugar beets following fermentation of starch and condensation of lactic acid. PLA offers great promise in a wide range of commodity applications and competes with polystyrene for many food packaging applications. It is a highly transparent and rigid material with a relatively low crystallization rate that makes it a promising candidate for the fabrication of biaxially oriented films, thermoformed containers and stretch-blown bottles (Dorgan, Lehermeier, & Mang, 2000; Yew, Mohd Yusof, Mohd Ishak, & Ishiaku, 2005). Comparing to some petro-chemical based polymers, PLA has some weaknesses; the oxygen and moisture permeability of PLA is much higher than for most other plastics, such as PE, PP, and even PET. PLA applications are also limited by several factors such as low glass transition temperature, weak thermal stability, and low toughness and ductility (Harada et al., 2007). PLA has the ability to be tailor-made for the properties needed for special applications (Arvanitoyannis, 1999).

There are many research studies focusing on PLA modification for extending PLA applications. Properties like impact strength or flexibility, stiffness, barrier properties and thermal stability can be improved by the addition of modifiers, blending, copolymerizing and physical treatments. Citrate esters, triacetine, tributyl citrate, oligomeric malonate esteramides, 4,4-methylene diphenyl diisocyanate, polyglycerol esters, polyethylene glycol, acetyl triethyl citrate, talc, bifunctional cyclic ester, poly(1,3-butylene adipate) have been studied as PLA modifiers (Jamshidian, Tehrany, Imran, Jacquot, & Desobry, 2010).

The additives used for PLA modification are limited by the requirements of the application. For food packaging and hygiene applications, only nontoxic substances approved for food contact and personal care can be considered as modifying agents. Additionally, the modifiers should be miscible with PLA, thus creating a homogeneous blend but should not be too volatile because this would cause evaporation to occur at the elevated temperatures used at processing. The migration of modifiers form PLA should also be considered to minimize the contamination of the food in contact with the modified PLA (Ljungberg & Wesslén, 2002). As migration of additives from polymers in contact with foodstuffs is not usually zero, so one logical way of modifying PLA is to use compounds which are usually consumed in foods such as permitted natural or synthetic antioxidants, natural antimicrobial agents like nisin, and so on. In this case if the modifying agents migrate

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Table 1
Summary of researches based on impregnation of antioxidants to polymers.

Object	Antioxidant(s)	Polymer	Reference
Migration to food simulants	BHT	HDPE	Till et al. (1982)
Mobility in polymer in contact with fatty food simulants	α-Tocopherol, BHT	LDPE	Wessling, Nielsen, Leufvén, and Jagerstad (1998)
Retention in polymer in contact with foodstuffs and food-simulating liquids	α-Tocopherol	LDPE, PP	Wessling, Nielsen, Leufvén, and Jagerstad (1999)
Influence of antioxidant on the polymer properties	α-Tocopherol	LDPE	Wessling, Nielsen, and Leufvén (2000)
Stability of antioxidant in packaging film used for oatmeal	α-Tocopherol, BHT	LDPE	Wessling et al. (2001)
Migration of phenolic antioxidants from branch and linear polymer	Santonox, Irganox 1081, Low inox 22M46	PE	Lundback, Hedenqvist, Mattozzi, and Gedde (2006)
Antioxidant migration study of some polymers	BHA, BHT, AO 2246, Ethanox 330, Irganox 1010, Irganox 1076	LDPE, HDPE, PP, PVC, PET	Dopico-Garciǐa et al. (2007)
Antioxidant migration into food simulants	Irgafos 168, Irganox 1076	LLDPE	Jeon, Park, Kwak, Lee, and Park (2007)
Release of antioxidants to dry milk products and food simulants liquids	α-Tocopherol, BHA, BHT	PLGA	Van Aardt et al. (2007)
Release of antioxidant to asadero cheese and its effect on oxidation and odor stability	BHT	LDPE	Soto-Cantú et al. (2008)
Improving antioxidant release by smart blending	α, β, and δ-tocopherols	LLDPE:HDPE LLDPE:PP LLDPE:PS	Schaich, Obinata, and Yam (2008)
Release of antioxidant from polymer film to whole milk powder	α-Tocopherol, BHA, BHT	HDPE–EVA–LDPE (co-extruded)	Granda-Restrepo, Peralta, Troncoso-Rojas, and Soto-Valdez (2009)
Release of antioxidant from polymer film to distilled water	L-Ascorbic acid, L-tyrosine	CA	Gemili, Yemenicioglu, and Altinkaya (2010)

HDPE, high density polyethylene; LDPE, low density polyethylene; LLDPE, low linear density polyethylene; PE, poly ethylene; PP, poly propylene; PVC, poly vinyl chloride; PET, polyethylene terephthalate; PLGA, poly(lactide-co-glycolide); EVA, ethylene vinyl acetate; CA, cellulose acetate.

to food, the safety concerns regarding to release of unpermitted agents do not occur and released compounds can act as preservatives resulting in some types of active packaging. The addition of synthetic antioxidants in polymer formulations is a common practice as a way to protect polymeric degradation during processing and also during their life-time. Antioxidants protect the polymer against the formation of undesirable oxidative and low molecular compounds which can migrate to foods causing a decrease in food quality. However, the potential migration of these substances to the packaged product has been an issue that should be considered to maintain food quality and safety (Dopico-Garciǐa, Loǐpez-Vilarin͂oǐ, & Gonzaǐlez-Rodriǐguez, 2007; Garde, Catala, Gavara, & Hernandez, 2001).

Oxidation produces low-molecular-weight off-flavor compounds, destroys essential nutrients, and produces toxic compounds and dimmers or polymers of lipids and proteins (Aruoma, 1998). In fats and oils, antioxidants delay the onset of oxidation or slow the rate of oxidizing reactions. The main purpose of using an antioxidant as a food additive is to maintain the quality of that food and to extend its shelf life rather than improving the quality of the food. Since free radicals were found to be responsible for lipid oxidation, hundreds of natural and synthetic compounds have been evaluated for their efficacy as radical scavengers or for their other inhibitory effects. Among them, only four synthetic antioxidants are widely used in foods; namely, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), and tert-butylhydroquinone (TBHQ) (Wanasundara & Shahidi, 2005).

Apart from the modifying effects of antioxidants for polymers, antioxidant-active packaging is an important category of active packaging and promising technique for extending food shelf life, different antioxidants have been impregnated in several polymer films and their migrations in real foods and food simulants have been studied. In some cases, the effects of migrated antioxidants on lipid oxidation and odor stability have also been investigated (Table 1), but in most studies important objectives were rates, effects, and mechanisms of antioxidants' release. Mechanical, physicochemical and barrier properties affect technical properties and stability of polymer in various conditions and structural properties can influence the rate and amount of active agents whom desired to migrate. The first group of properties is routinely examined in using modifying compounds but structural properties are rarely studied. Atomic force microscopy (AFM) technique can provide precise information about morphological changes made by modifiers which can affect their release to food stuffs (Kikkawa, Fujita, Abe, & Doi, 2004; Sanchez-Garcia, Gimenez, & Lagaron, 2008). X-ray photoelectron spectroscopy (XPS) determines chemical composition of the surface layer and characterizes possible chemical bonding between the modifying agent and the polymer (Kiss, Bertóti, & Vargha-Butler, 2002).

Recently, Byun, Kim, and Whiteside (2010) studied the addition effect of α-tocopherol and polyethylene glycol 400 (PEG 400) on film-cast-extruded PLA. The authors concluded that the addition of PEG 400 as a plasticizer decreases the T_g, and tensile strength of the film and reversely increases % elongation at break. They showed the incorporation of α-tocopherol into PLA film increases oxygen permeability and decreases water vapor permeability (WVP) of the PLA film. Lopez-Rubio and Lagaron (2011) characterized UV stability and mechanical properties of some biopolyesters including PLA, PCL (polycaprolacton) and polyhydroxybutyrate-co-valerate (PHBV) containing β-carotene. They showed a plasticizing effect of β-carotene resulting in significant increase in the deformation at break and lower Young's modulus. The results confirmed even though UV radiation degraded β-carotene in polyesters but their mechanical properties remained more stable than those of the pure polymers suggesting β-carotene as a natural additive to increase the UV stability of biopolyesters. The authors used Raman spectroscopy to study the dispersion and degradation of β-carotene in selected areas of the different biopolyester films.

The addition of active compounds may affect the structure and other physical and mechanical characteristics which are important in respect to technological and functional aspects of packaging materials, so an active packaging without desired applied 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 active compound and polymer structure which may be inapplicable in some cases. To our knowledge the effects of synthetic phenolic antioxidants (SPAs) on PLA physical, mechanical and structural properties in one hand for its modification and in the other hand for providing an antioxidant-PLA packaging have not been well investigated before, so the aim of this study focused on characterizing the addition effects of SPAs including BHA, BHT, PG, and TBHQ on physical, structural, mechanical, thermal, and gas barrier properties of PLA.

2. Materials and methods

2.1. Materials

Poly (lactic acid) (PLA), 2002 D, was purchased in pellet form from Natureworks® Co., Minnetonka (USA); Chloroform D (99.8% $CDCL_3$) from Euriso-Top (France); Magnesium nitrate, phosphorus pentoxide, BHA, BHT, PG, and TBHQ from Sigma–Aldrich (France); Chloroform HPLC grade and potassium nitrate from VWR international (France).

2.2. Film preparation method

For each film containing 1% of antioxidant, a solution of 3.5% (w/w) of PLA was prepared in chloroform and afterwards 1% (w/w) of antioxidants based on PLA dry matter were added to solution and mixed for 1 h for complete solution of antioxidants in polymer matrix. Then 20 g of polymer solution was cast in Teflon 90 × 110 mm Petri dishes (Welch, USA) the extra chloroform was evaporated in a dark place under hood during 24 h at 25 °C then films were placed in incubator (Memmert, Germany) at 30 °C for 7 days for complete solvent evaporation. The Petri dishes were kept in a hermetic container containing P_2O_5 powder before each analysis. The final film thickness was 100 ± 5 μm measured (at least 8 points) by a mechanical micrometer (Messmer, UK) according to ASTM D374.

2.3. Determination of SPAs in PLA films

The amounts of SPAs 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 $CDCL_3$ and SPAs amount were quantified by comparing the peak area of each antioxidant in a sample with the one of the corresponding peak of the standard at a known concentration. Standard precautions regarding quantization in NMR were taken including identical spectrometers settings, repetition time between two consecutive scans long enough in comparison with relaxation times. All tests were accomplished in triplicate.

2.4. Thermal properties

Thermal analysis for measurement of transition temperatures including glass transition temperature (T_g) and melting temperature (T_m), and enthalpies of fusion (ΔH_f) and crystallization (ΔH_c) was carried out with a differential scan calorimeter (NETZSCH, Germany). Specimens weighing 10 mg were sealed in an aluminum pan and heated under protective nitrogen (40 ml min^{-1}) at the rate of 10 °C min^{-1} from 5 to 210 °C then cooled to 5 °C and reheated to 210 °C with the same cooling–heating rate.

T_g, T_c and T_m were determined form the obtained thermogram. The degree of crystallinity was evaluated according to Eq. (1):

$$\%\,\text{Crystallinity} = 100 \times \frac{\Delta H_m - \Delta H_c}{\Delta H_f} \quad (1)$$

where ΔH_f is the enthalpy of fusion; ΔH_c is the enthalpy of crystallization; and ΔH_m is the enthalpy of fusion of a wholly crystalline PLA (93.6 J/g) (Arnoult, Dargent, & Mano, 2007).

2.5. Mechanical properties

A Lloyd instruments testing machine (AMETEK, UK) was used to determine different mechanical properties including tensile strength, Young's modulus and percent of elongation at break according to ASTM D882. Before testing, all samples were equilibrated for 48 h at $50 \pm 2\%$ relative humidity (RH) in a container using magnesium nitrate saturated solution at 20 ± 1 °C. Equilibrated film specimens were mounted in the film-extending grips of the testing machine and stretched at a rate of 25 mm min^{-1} until breaking. The RH and temperature of the testing environment was held at $52 \pm 2\%$ and 20 ± 2 °C, respectively.

2.6. Water vapor permeability (WVP) measurement

The Water vapor transition rate (WVTR) measurements were done using a Permatran W3/31 (Mocon, Inc., Minneapolis, MN, USA) according to ASTM standard F1249 (ASTM, 1995). The calibration of the instrument for WVTR measurements was performed using polyester standard films provided by Mocon. Water vapor concentration within the nitrogen stream is measured by an infrared detector contained within the instrument. Samples were exposed to 90% RH and tested at 38 ± 1 °C. Water vapor permeability ($\text{kg m m}^{-2}\,\text{s}^{-1}\,\text{Pa}^{-1}$) was calculated by multiplying the WVTR by film thickness. The tests were done in triplicate and the mean values were reported.

2.7. Oxygen permeability measurement

The oxygen transition rate (OTR) measurements were accomplished using an OX-TRAN 2/21 (Mocon, Inc., Minneapolis, MN, USA) according to ASTM standard D3985 (ASTM, 1995). Measurements were conducted at 23 ± 1 °C and 0% RH. Flat films were clamped into the diffusion cell that was purged of residual oxygen using an oxygen-free air carrier gas. The carrier gas was routed to the sensor until a stable zero was established. Pure (99.9%) oxygen was then introduced into the outside chamber of the diffusion cell. Oxygen permeability ($\text{m}^3\ \text{m m}^{-2}\,\text{s}^{-1}\,\text{Pa}^{-1}$) was calculated by multiplying the OTR by film thickness. Tests were done in triplicate with the mean values were reported.

2.8. Surface characterization

2.8.1. Measurement of contact angle

The contact angle of the films was obtained at 20 °C using a commercial Digidrop meter (GBX Scientific Instruments, France) equipped with a charge-coupled device (CCD) camera 2/3″ and a Nikon 60 mm macro lens. This apparatus comprises the software named Windrop^{++} which precisely determines the drop size of the liquid placed on the sample surface. The contact angle was measured by adding randomly 10 drops of ultra pure liquids (2 μl) on the surface of a film disk (80 mm in diameter). Using Windrop^{++} software provided with instrument, measurements of the static contact angle values were fully automated.

2.8.2. Measurement of surface energy

The total surface energy of PLA films were graphically determined using same Digidrop meter apparatus by the method of Owens–Wendt which usually used for solids with low surface energy such as polymers. For this measurement, 4 special liquids including, water, glycerol, ethylene glycol and diiodomethane were used. The Owens–Wendt theory divides the surface energy into two components: surface energy due to dispersive interactions and surface energy due to polar interactions. Owens and Wendt proved that the total surface energy of a solid, γ_s, can be expressed as the sum of contributions from dispersion γ_s^d and polar γ_s^p force components ($\gamma_s = \gamma_s^d + \gamma_s^p$). These can be determined from the contact angle, θ, data of polar and non-polar liquids with known dispersion γ_L^d and polar γ_L^p parts of their surface energy, via Eq. (2) (Awaja, Gilbert, Kelly, Fox, & Pigram, 2009; Michalski, Desobry, & Hardy, 1998):

$$\gamma_L(1 + \cos\theta) = 2\sqrt{\gamma_L^d \gamma_s^d} + 2\sqrt{\gamma_L^p \gamma_s^p} \tag{2}$$

where γ_L is the liquid surface tension.

2.8.3. X-ray photoelectron spectroscopy (XPS)

The XPS analyses were carried out with a Kratos Axis Ultra spectrometer (Kratos Analytical, Manchester, UK) using a monochromatic Al Kα source. All spectra were recorded at 90° take-off angle and analyzed area was about 700 μm × 300 μm. Survey spectra were recorded with 1.0 eV step and 160 eV analyzer pass energy and the high resolution regions with 0.1 eV step and 20 eV pass energy, with an exception for the carbon with 0.05 eV step. In both cases the hybrid lens mode was employed (magnetic and electrostatic). During the data acquisition the Kratos charge neutralizer system was used on all specimens with the following settings: filament current 2 A, charge balances 3.5 V, filament bias 1.0 V and magnetic lens trim coil 0.34 A. The C–(C, H) carbon was set to 284.60 eV and therefore used as an internal energy reference.

Spectra were analyzed using the Vision software from Kratos (Vision 2.2.6). A Shirely base line was used for the subtraction of the background from each peak. Quantification was performed using the photoemission cross sections and transmission coefficients given in the Vision package.

2.8.4. Atomic force microscopy analysis (AFM)

The surface morphology was analyzed by using a D3100 AFM equipped with a Nanoscope 5 electronic from Veeco manufacturer. The images were recorded at ambient conditions (20 °C and 30% RH) and in soft intermittent contact mode (IC-AFM or Tapping^{TM} AFM). Tap150 tapping mode cantilevers (Veeco model No MPP-12100) with a typical spring constant of about 5 N/m and a resonance frequency around 165 kHz was used for scanning. Tapping force was controlled by the ratio between set point amplitude (A_{sp}) and free-air amplitude (A_0). The scan rate was adjusted in the range of 0.5–1 Hz depending on the image quality. Each scan line contains 512 pixels and a whole image is composed of 512 scan lines. For acquisition of the surface morphology amplitude error, phase and height images were recorded on several areas of film surface. Only the representative height images were presented here for discussion with a scan size of 20 μm^2, 10 μm^2, 5 μm^2 and 2 μm^2 for PLA–BHT, PLA–BHA, PLA and PLA–PG, and PLA–TBHQ, respectively.

All offline image flattening and analyses of the images were conducted at the software environment provided by the AFM manufacturer. The statistical parameters related with sample roughness (ASME B46.1, 1995) were estimated by the software equipment in a 2 μm^2 area at the center of AFM image, so average roughness (R_a) and root mean square roughness (R_q) were only presented.

Table 2
Thermal properties of PLA films containing 1% SPAs.

	T_g	T_c	T_m	% Cryst.
PLA–BHA	54.3 ± 1.0^a	98.4 ± 3.6^{ac}	143.4 ± 0.7^a	13.8 ± 1.5^a
PLA–BHT	55.1 ± 0.9^a	97.6 ± 0.8^{ac}	143.3 ± 0.1^a	14.3 ± 0.6^a
PLA–PG	55.8 ± 0.8^a	100.4 ± 2.8^c	140.1 ± 0.1^b	14.8 ± 1.62^a
PLA–TBHQ	54.6 ± 0.8^a	95.3 ± 1.8^a	140.8 ± 1.1^b	14.1 ± 1.1^a
Pure PLA	55.3 ± 0.7^a	107.0 ± 0.8^b	144.7 ± 0.3^c	19.5 ± 0.5^b

The means of three replicates plus or minus the standard deviation are shown. Significant difference ($P \leq 0.05$) is represented by different alphabetic letters.

2.9. Statistical analysis

The data were analyzed by analysis of variance (ANOVA) using StatGraphics (version 16, StatPoint Technologies, Inc., Warrenton, VA, USA) and differences among mean values were processed by the Student–Newman–Keuls multiple range test. Multiple comparisons were performed through 95% least significant difference intervals ($P \leq 0.05$).

3. Results and discussion

3.1. SPAs amounts in PLA films

NMR data showed decrease amounts of SPAs in PLA films. PLA films loaded with 1% (wt%) SPAs yielded a recovery of 90%, 87%, 85% and 80% for TBHQ, BHT, BHA, and PG respectively. The 23% lost of BHA and BHT in poly(lactide-co-glycolide) (PLGA) films due to their evaporation has been reported (Van Aardt et al., 2007). The volatility of antioxidants is desired for dried food applications because of their rapid migration via evaporation from polymer surface to target food (Wessling, Nielsen, & Giacin, 2001).

3.2. Thermal properties

Fig. 1 presents a DSC thermograph of pure PLA, PLA–BHA and PLA–TBHQ films. DSC results of five different PLA films containing 1% SPAs and pure PLA are presented in Table 2. The pure PLA exhibited a T_g around 55 °C and a melting temperature (T_m) around 144 °C. Calculated PLA crystallinity according to equation 1 was 19.5% and crystallization temperature (T_c) around 107 °C. In each DSC curve, only a single exothermic crystallization peak, T_c, appears which suggests a single crystallization process during the dynamic cooling procedure. Therefore, the distribution of the crystallites size such a melt-crystallized sample is believed to be unimodal instead of bimodal. Consequently, the occurrence of double melting peaks during the subsequent heating scan is not associated with the possibility of bimodal size distribution of the crystallites (Ling & Spruiell, 2006). The double melting peak of PLA has been attributed to a melting-recrystallization phenomenon where the lower endotherm corresponds to the melting of initially present crystals. The partially molten material is thought to be able to recrystallize into more perfect α-crystals polymorph melting at higher temperature in the second endotherm (Sarasua, Zuza, Imaz, & Meaurio, 2008). The double melting endotherm was more pronounced for films containing SPAs demonstrating the various effect of SPAs on melting-recrystallization behavior, for example the height of first melting peak of PLA–BHA is smaller than the second one while for PLA–TBHQ the height of first melting peak is larger than the second one.

The addition of the antioxidants reduced the crystallization temperature by 6–12 °C from the value of 107 °C found for pure PLA film. All SPAs equally reduced the crystallinity by about 26%; they also slightly reduced the T_m but had no significant effect on T_g. It seems that SPAs somehow hinder polymer chains lateral rearrangements and hence crystallization in PLA. These similar effects

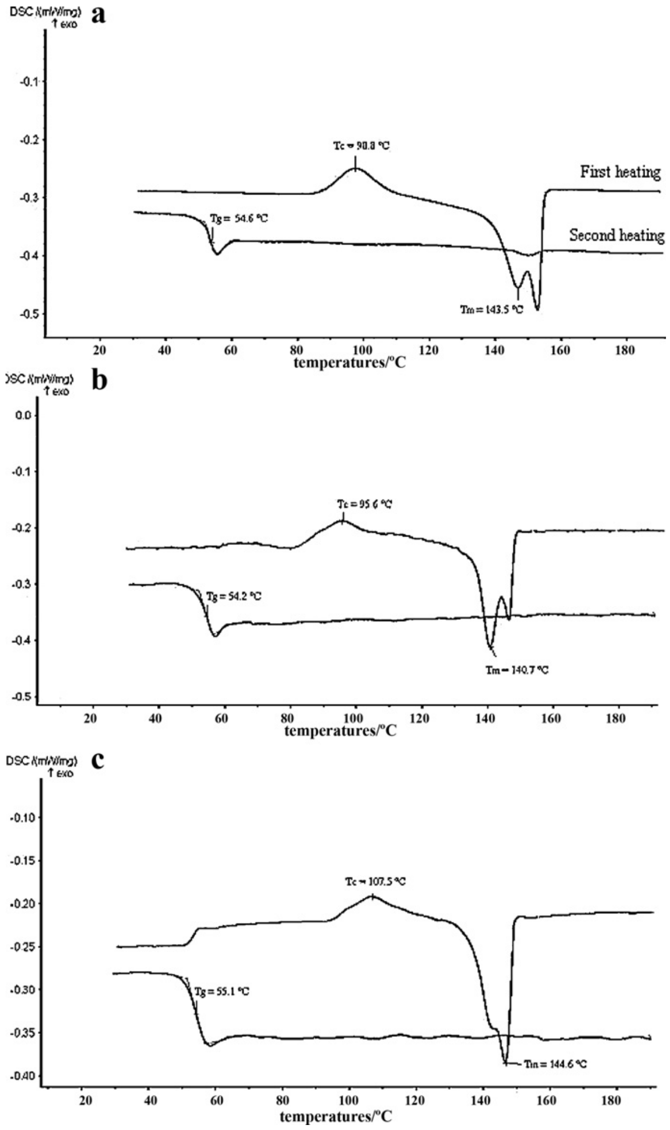

Fig. 1. DSC thermograph of PLA films, *a* = PLA–BHA, *b* = PLA–TBQ and *c* = pure PLA.

were observed for cellulose fiber and β-carotene in PCL and PHBV, respectively (Lopez-Rubio & Lagaron, 2011; Sanchez-Garcia et al., 2008). Reduction of crystallinity is a negative point in the aspect of mechanical and barrier properties and positive point for PLA rapid biodegradation in nature or in biomedical applications. In many applications, increasing the crystallization amount of PLA is desired because in its amorphous form, the range of application of PLA is severely limited by its low glass transition temperature. Thus for these cases the crystalline form is required to increase the high temperature stability of PLA (Li & Huneault, 2007). Addition of modifiers such as 4,4-methylene diphenyl diisocyanate (Li & Yang, 2006), increases T_g of PLA and other studies confirmed some modifications in PLA thermal properties by blending or copolymerizing (Dorati et al., 2007; Jang, Shin, Lee, & Narayan, 2007; Quan, Liao, & Zhao, 2004).

3.3. Mechanical properties

Young's modulus, tensile strength and % elongation at break are three important factors for studying the mechanical properties of polymeric films. The mechanical properties of PLA films containing 1% SPAs is represented in Table 3. Young's modulus and tensile strength of PLA film were reduced by addition of BHA, PG and TBHQ. Young's modulus was reduced 12% by BHA and 17% by PG and TBHQ. These three antioxidants had also a reducing effect on tensile strength; 14% by BHA and 20% by PG and TBHQ. Only BHT had no negative effect on PLA mechanical properties. It is well known that PLA crystallinity can play a significant role in the mechanical and durability performance in rigid molded applications. An increase in the polymer's overall crystallinity can lead to improvements in stiffness, strength, heat deflection temperature and chemical resistance (Harris & Lee, 2008). PLA crystallinity has also a direct effect on tensile strength and Young's modulus properties; as be seen in Table 2 the PLA crystallinity is reduced by SPAs and the relation between crystallinity and tensile strength of PLA films containing 1% SPAs is well demonstrated in Fig. 2, in reducing the % crystallinity Young's modulus and tensile strength were decreased. Changes in polymer matrix or reduction of polymer homogeneity due to SPAs addition can also affect these mechanical parameters and could be the reason of these behaviors. In the case of PLA–BHT Young's modulus and tensile strength were not changed despite of reduced amount of crystallinity proposing the participation of other factor(s) made by BHT addition on PLA structure neutralizing the negative effect of crystallinity reduction. Complementary studies using microscopy methods can provide more information about BHT incorporation in PLA matrix. SPAs did not change the % elongation at break presenting no plasticizing effect of SPAs on PLA. Rhim, Mohanty, Singh, and Ng (2006) showed the PLA films prepared by the thermocompression method had higher modulus and strength but lower toughness than PLA films prepared by solvent-casting method. They showed that the elongation at break of PLA films prepared by solvent-casting and thermocompression is about 203% and 3%, respectively. This high value of elongation was reported due to existence of chloroform (about 13%) in solvent-cast film which acts as a plasticizer. In this study the film solution drying prolonged for 7 days at 30 °C ensured no solvent existence in the final films and no plasticizing effect of chloroform.

Table 3
Mechanical properties of PLA films containing 1% SPAs.

	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PLA–BHA	1.96 ± 0.10^{a}	49.6 ± 3.5^{ac}	3.4 ± 0.2^{a}
PLA–BHT	2.17 ± 0.07^{b}	54.7 ± 3.5^{bc}	3.0 ± 0.4^{a}
PLA–PG	1.85 ± 0.08^{a}	46.9 ± 2.6^{a}	3.2 ± 0.4^{a}
PLA–TBHQ	1.85 ± 0.08^{a}	45.8 ± 3.2^{a}	3.3 ± 0.2^{a}
PLA	2.24 ± 0.04^{b}	58.0 ± 2.8^{b}	3.6 ± 0.2^{a}

The means of at least six replicates plus or minus the standard deviation are shown. Significant difference ($P \leq 0.05$) is represented by different alphabetic letters.

The addition effects of different compounds on PLA mechanical properties have been largely studied; citrate esters (Labrecque, Kumar, Davé, Gross, & McCarthy, 1997), oligomeric malonate

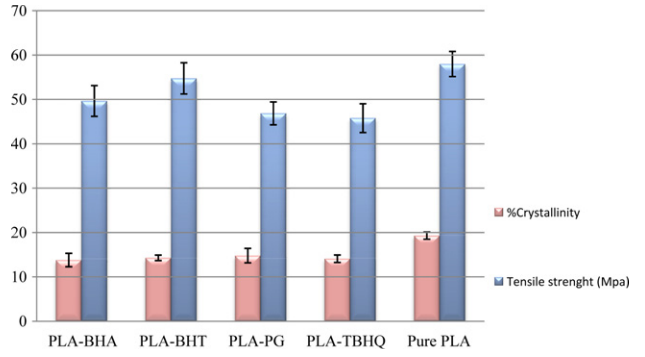

Fig. 2. Tensile strength and % crystallinity of PLA and PLA films containing 1% SPAs.

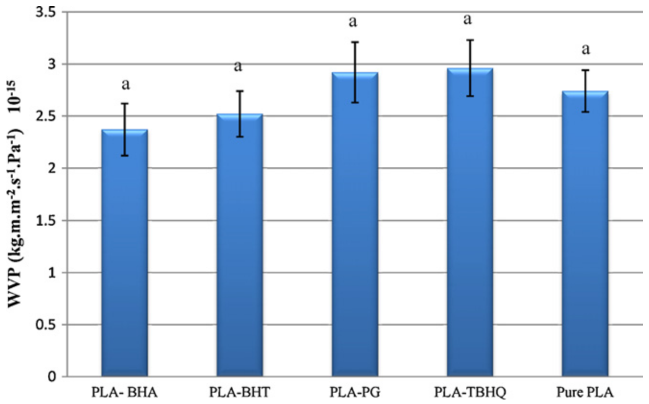

Fig. 3. WVP of PLA and PLA films containing 1% of SPAs at 38 °C and RH = 90% (all measurements were performed in triplicate).

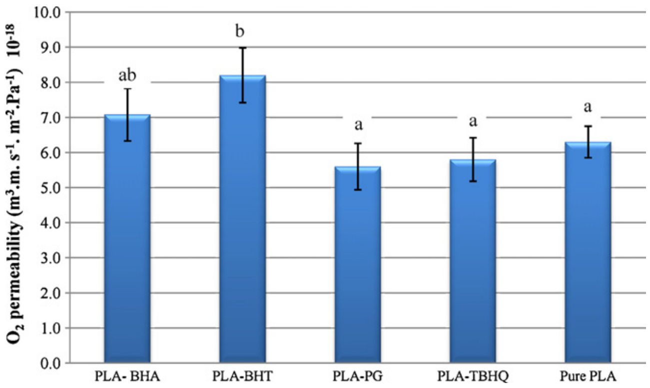

Fig. 4. Oxygen permeability of PLA films containing 1% of SPAs at 23 °C and RH = 0% (all measurements were performed in triplicate, significant difference ($P \leq 0.05$) is represented by different alphabetic letters).

esteramides (Ljungberg, Colombini, & Wessleén, 2005), 4,4-methylene diphenyl diisocyanate (Li & Yang, 2006), bifunctional cyclic ester (Jing & Hillmyer, 2008), poly(1,3-butylene adipate) (Wang, Zhang, Yu, & Fang, 2008) have been shown to have the ability to modify the tensile strength values of PLA. Blending, copolymerizing and physical treatment have also been studied to increase the tensile strength of PLA (Gajria, Davé, Gross, & McCarthy, 1996; Grijpma, Altpeter, Bevis, & Feijen, 2002; Kylmä, Härkönen, & Seppälä, 1997; Li & Shimizu, 2009; Nijenhuis, Colstee, Grijpma, & Pennings, 1996; Todo, 2007). However, there are always some differences in mechanical and barrier properties of solvent-cast and extruded films.

3.4. *WVP*

WVP is one of the most important properties in food packaging mainly because of the significant role of water in deteriorative reactions and also microbial growth. Water acts as a solvent or carrier, causes textural degradation, and provides chemical and enzymatic reactions. WVP of PLA and PLA films containing 1% SPAs are shown in Fig. 3. SPAs addition had no significant effect on WVP of PLA. Crystallinity has an important effect on WVP because the crystallites themselves are impermeable. Thus, water vapor must seek out amorphous zones in order to penetrate in polymer. In the case of SPAs the 26% reduction of crystallinity had no noticeable influence on WVP. Tsuji, Okino, Daimon, and Fujie (2006) showed that the water vapor transition rate (WVTR) of PLA films decreased monotonically with increasing the crystallinity (X_c) from 0 to 20%, while leveled off for X_c exceeding 30%. They assumed that this is probably due to the higher resistance of “restricted” amorphous regions to water vapor permeation compared with that of the “free” amorphous regions.

3.5. *Oxygen permeability*

The oxygen permeability of PLA films containing 1% SPAs is presented in Fig. 4. Oxygen permeability of extruded PLA given in literature data is between 1.9×10^{-18} and $6.0 \times 10^{-18}\ \mathrm{m^3\,m\,m^{-2}\,s^{-1}\,Pa^{-1}}$ for various experimental setups (Auras, Harte, & Selke, 2004; Auras, Singh, & Singh, 2005; Colomines, Domenek, Ducruet, & Guinault, 2008; Sanchez-Garcia, Gimenez, & Lagaron, 2007). Our results even though obtained from solvent cast films are consistent with those data. BHT increased PLA oxygen permeability by 30%. The bars in oxygen permeability graph imitate the tensile strength and Young’s modulus bars showing the influence of BHT on PLA structure, while BHA, PG and TBHQ did not change the PLA oxygen permeability. Like WVP, oxygen permeability decreases with increasing crystallinity in polymers. Generally, this is because gases cannot diffuse and permeate in the crystalline phase and small molecules only pass through the amorphous region because the polymer chain mobility is considerably restricted in the crystalline phase, leading to difficult diffusion and dissolution (George & Thomas, 2001). The decrease about 26% of PLA crystallinity caused by antioxidant could not have a great effect on oxygen permeability because all PLA films containing antioxidants have a similar crystallinity but PLA–BHT has a higher oxygen permeability explaining other influencing factors. In some cases the crystallinity has a reverse effect leading to higher oxygen permeability because of the phenomenon of de-densification of the amorphous phase which counteracts the decrease of the quantity of permeable amorphous phase due to crystallization (Liu, Hu, Schiraldi, Hiltner, & Baer, 2004). Colomines et al. (2008) reported that the quenched PLA film containing 39% crystallinity had higher oxygen permeability than PLA film containing 2% crystallinity; so they hypothesized the PLA de-densification during quenching treatment.

By considering the SPAs molecular structure and their physic-chemical properties such as molar volume and surface area it is possible to interpret the BHT effect on oxygen permeability. One factor which can play an important role is antioxidant volume and therefore its occupied space in polymeric network; more occupied space provides less polymer orientation and more oxygen permeability. Molecular volumes of SPAs were calculated by Molecular Modeling Pro$^{\mathrm{TM}}$ 5 (Fig. 5). As BHT has a more open structure so its molecular volume is higher than other antioxidants facilitating the oxygen passage. Using Henry’s law describing the gas solubility in a polymer and Fick’s laws that characterize the gas diffusion in that material, the gas permeability may be expressed as a function of both solubility and diffusion coefficients, so it can be proposed that BHT increases oxygen diffusion in PLA film. A little increment in oxygen permeability influenced by BHA can be also attributed to its higher molecular volume rather than PG and TBHQ.

3.6. *Contact angle and surface energy*

The surface energy of a polymer influences its adhesive properties, and is important for processes such as printing and heat sealing. The contact angle, surface energy, polar component and dispersive component of PLA films with and without antioxidants have been presented in Table 4. As can be observed in this table, the contact angle of the PLA film with antioxidant slightly increases from 75.3° to the highest value 78.4° for PLA–TBHQ. This increment can be made because of hydrophobic nature of these antioxidants. The influence of SPAs on contact angle is not great because of two reasons, firstly because of their little added amounts (1%) to PLA

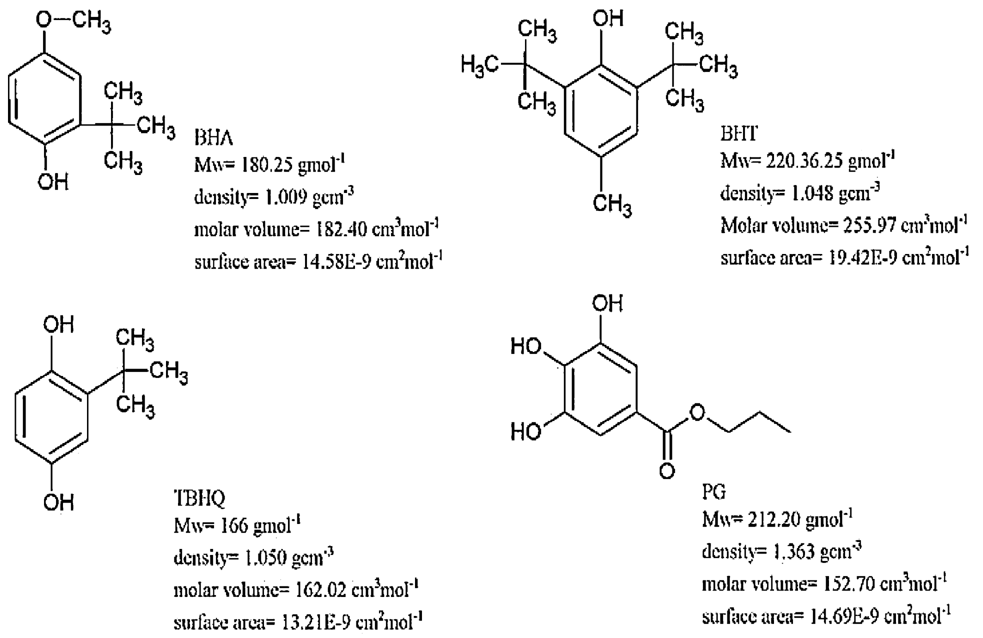

Fig. 5. Chemical structure and properties of synthetic phenolic antioxidants (molar volume and surface are calculated by Molecular Modeling Pro^{TM} 5).

and secondly because their total distribution occurred throughout the polymer network not only on its surface. The light increase in PLA contact angle by adding the SPAs, demonstrates the decreased wettability, suggesting that the PLA surfaces contain an increased number of hydrophobic groups after adding these antioxidants. The PLA hydrophobicity is desired for printing practices and plasma treatments is a usual way for modifying this property (Chaiwong, Rachtanapun, Wongchaiya, Auras, & Boonyawan, 2010). According to Table 4, the surface energy composed to polar and dispersive components; no significant changes were observed in the surface energy of PLA samples due to the addition of BHA, BHT and PG. However, TBHQ slightly decreased the PLA surface energy by reducing both dispersive and polar components. The surface energy of a polymer will influence its adhesive properties, and it is also important for processes such as printing and heat sealing.

3.7. XPS

XPS analysis was performed to examine the energy changes and chemical binding states of the polymer surfaces. Fig. 6 shows the C 1s and O 1s XPS spectra of the PLA film. The C and O peaks decomposed according to a model for biochemical compounds (Gerin, Dengis, & Rouxhet, 1995). The C 1s peak decomposed in three distinct peaks: a peak at 284.7 eV due to carbon atoms only bound to carbon and hydrogen (C–(C, H)), a second component was observed at 286.8 eV, attributed to carbon singly bound to oxygen (C–O) and the third at 288.8 eV due to carboxyl functions (C═O). The O 1s peak decomposed in two peaks attributed to the O═C, O–H at 531.3 eV and O–C at 532.7 eV. Table 5 presents the atomic composition of the PLA films before and after addition of antioxidants. SPAs had no significant effect on PLA surface atomic composition. As our XPS signal

Table 4
Contact angle and surface energy of PLA films containing 1% SPAs.

	Contact angle (°)	Surface energy (mJ/m^2)	Polar component (mJ/m^2)	Dispersive component (mJ/m^2)
PLA–BHA	77.2 ± 0.3^{a}	37.8 ± 1.4^{a}	5.1 ± 0.8^{ab}	32.7 ± 1.2^{a}
PLA–BHT	77.8 ± 1.4^{a}	37.1 ± 1.3^{a}	4.7 ± 0.6^{a}	32.4 ± 1.4^{ac}
PLA–PG	77.4 ± 1.1^{a}	35.4 ± 1.0^{ab}	6.1 ± 0.4^{b}	29.3 ± 0.8^{b}
PLA–TBHQ	78.4 ± 1.6^{a}	34.6 ± 0.9^{b}	6.1 ± 0.4^{bc}	28.6 ± 1.0^{b}
PLA	75.3 ± 1.6^{a}	36.3 ± 1.2^{a}	6.9 ± 0.5^{bc}	29.4 ± 1.6^{bc}

The means of three replicates plus or minus the standard deviation are shown. Significant difference ($P \leq 0.05$) is represented by different alphabetic letters.

Table 5
Atomic compositions and concentration of the different chemical bonds of PLA films containing 1% SPAs.

	O 1s	C 1s	Si 2p	C 1s C–(C, H)	C 1s C–O	C 1s O–C═O	O 1s O═C O–H	O 1s O–C	C/O
PLA recto	36.82	62.21	0.97	38.57	30.58	30.85	44.34	55.66	1.68
PLA verso	37.70	62.30	–	35.37	32.63	32.00	43.53	56.47	1.65
PLA–BHA recto	36.16	62.93	0.91	38.34	30.64	31.01	44.81	55.19	1.74
PLA–BHA verso	36.97	63.03	–	36.99	31.36	31.65	42.57	57.43	1.70
PLA–BHT recto	37.33	62.67	–	35.26	32.58	32.16	42.70	57.30	1.67
PLA–BHT verso	36.48	63.52	–	35.49	32.40	32.11	43.24	56.76	1.74
PLA–PG recto	36.99	62.07	0.94	37.87	31.09	31.04	45.82	54.18	1.67
PLA–PG verso	36.52	63.48	–	37.32	31.12	31.56	43.07	56.93	1.73
PLA–TBHQ recto	35.93	62.70	1.37	40.25	29.74	30.01	45.58	54.42	1.74
PLA–TBHQ verso	36.06	63.94	–	37.41	31.52	31.07	44.77	55.23	1.77

All the tests were carried out in duplicate, Standard deviations are not shown.

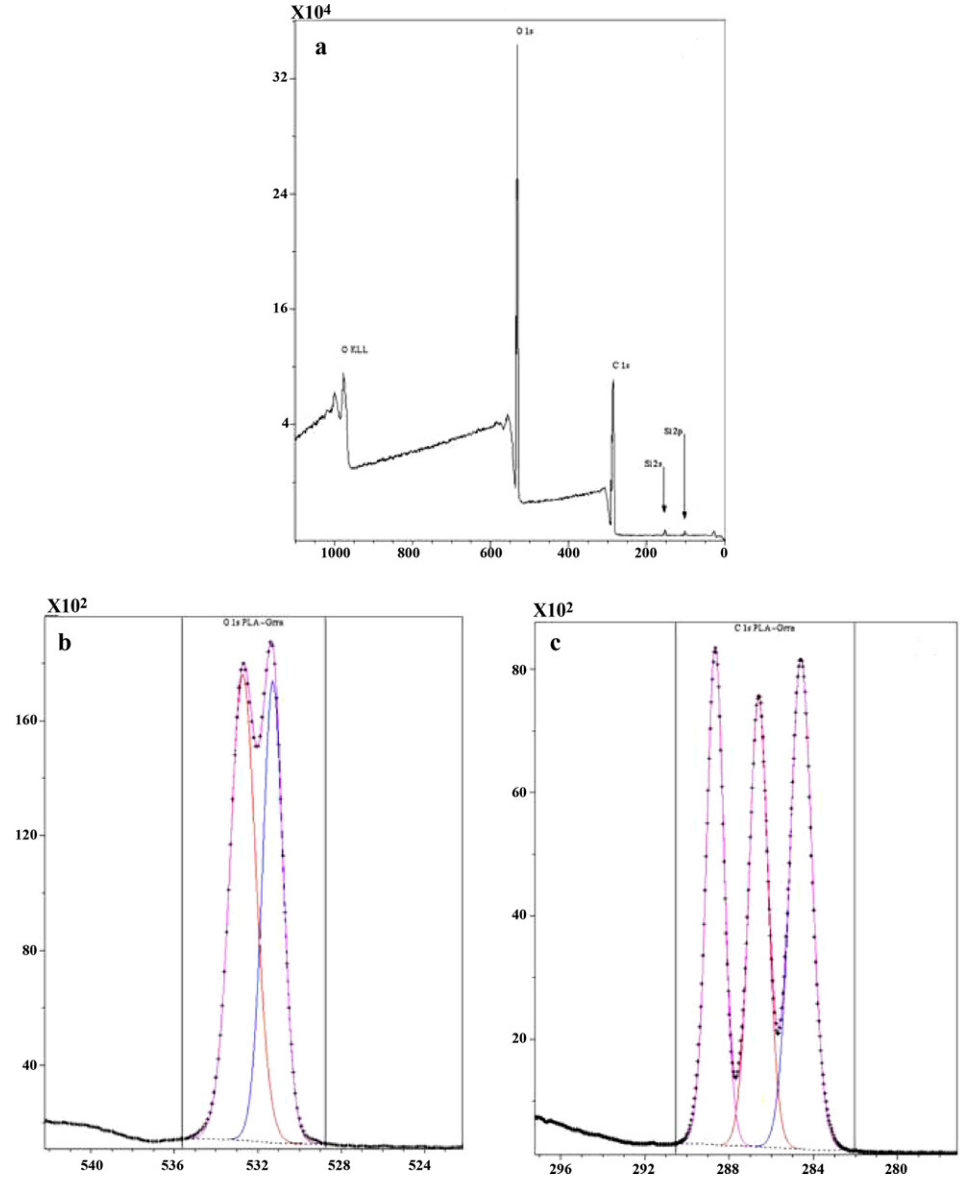

Fig. 6. XPS spectra obtained for PLA, a survey scan (a); narrow spectra of O 1s (b) narrow spectra of C 1s (c) levels. These peaks have been decomposed (see details in Section 3.6).

depth penetration was maximum 5 nm, it can be concluded that SPAs did not participate on extreme surface layer and distributed more in polymer matrix.

3.8. AFM results

Recently, tapping mode AFM has been used to investigate the surface structure and interactive force of nanostructured films (Jeong, Choi, Bae, Zentner, & Kim, 1999) and for instance to visualize crystalline morphology of poly(L-lactic acid) thin films (Li, Nie, Deng, Chen, & Ji, 2009). Therefore, in this study Intermittent Contact AFM (IC-AFM) was performed to get the better topographic images. AFM height images of PLA and PLA containing 1% SPAs thin films are displayed in Fig. 7. These images show that the surface microstructures of the films are drastically affected by adding the antioxidants.

PLA thin films (e) presented a homogenous smooth morphology with $R_a = 1.67$ nm and $R_q = 2.14$ nm. PLA–BHT (a) presents also a homogeneous microstructure which can be associated with well-ordering microfibrils. The surface roughness increased compared with PLA thin films ($R_a = 8.24$ nm and $R_q = 10.4$ nm).

Adding 1% of TBHQ induced fragmented microfibrils surface microstructure. Grain-like particles appeared with some remained rodlet shaped. Compared with PLA thin films, PLA–TBHQ thin films had a near similar roughness in order of 2.11 nm and 2.75 nm for R_a and R_q, respectively.

By adding 1% of BHA to PLA film, the roughness parameters, R_a and R_q, are decreased with 0.673 nm and 0.855 nm, respectively. It can be observed a drastically change in microstructure surface compared to PLA films containing BHT and TBHQ antioxidants. PLA–BHA surface presented two micro-domains certainly associated with a difference of mechanical properties, one like PLA surface microstructure and the other one like orange skin.

By adding 1% of PG, the surface microstructure varied significantly compared to other surfaces where ellipsoidal structures

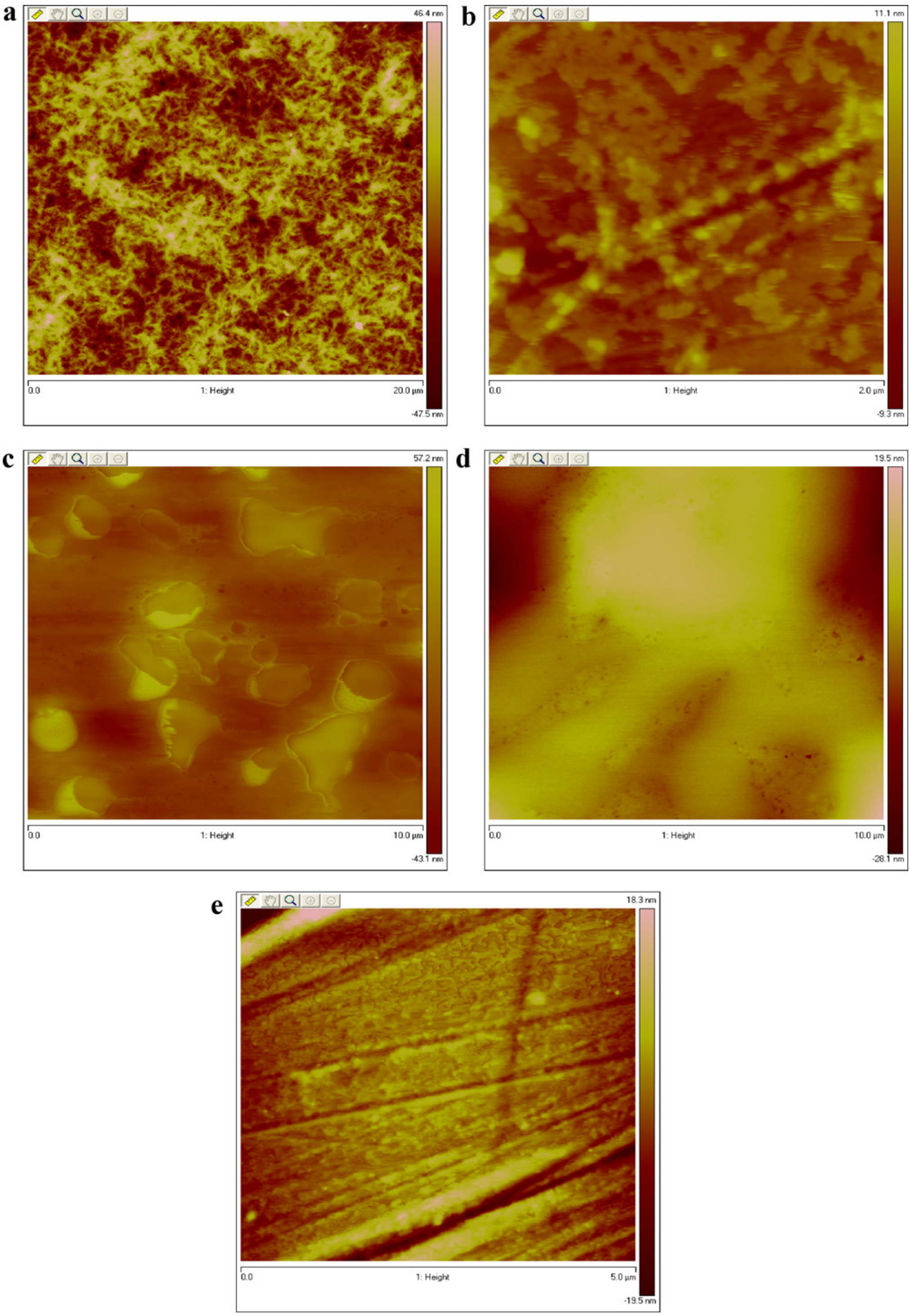

Fig. 7. AFM images of thin films, PLA–BHT (a), PLA–TBHQ (b), PLA–PG (c), PLA–BHA (d), and PLA (e).

with a flat center with a thickness in the order of 20 nm and axes $a \approx 1.3\,\mu\text{m}$ and $b \approx 2\,\mu\text{m}$ can be seen. It can be supposed that this organization could be attributed to atomic structure of PG antioxidants. The hypothesis should be confirmed in other work using for instance HarmoniX AFM mode (Hartman et al., 2010). As a matter of fact, the roughness of PLA–PG increased in comparing to PLA ($R_a = 1.67$ nm and $R_q = 2.14$ nm).

In term of roughness parameters (R_a and R_q), we can classify the surface morphology following to this order: PLA–BHT > PLA–PG > PLA–TBHQ > PLA > PLA–BHA.

4. Conclusion

In this study, it was shown that addition of 1% of SPAs to PLA film by casting method results in changing of some physical and mechanical characteristics including 26% reduction in PLA crystallinity by all SPAs. Young's modulus and tensile strength of PLA film were slightly affected by BHA, PG and TBHQ. WVP of PLA was not changed by 1% addition of SPAs but the oxygen permeability of PLA film was influenced just by BHT. It was concluded that open chemical structure of BHT and its higher molar volume can be considered as influencing factors. XPS results showed that two different faces of PLA films containing 1% of SPAs are not exactly the same and this suggested that SPAs are not uniformly distributed in film thickness because of partial antioxidant precipitation during polymer solution drying. Some microscopic methods such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are needed to investigate SPAs distribution in PLA matrix prepared by solvent-casting method. PLA film microstructures were significantly changed by addition 1% of SPAs; in term of roughness parameters (R_a and R_q), we can classify the surface morphology following this order: PLA–BHT > PLA–PG > PLA–TBHQ > PLA > PLA–BHA. In one hand, SPAs globally had not a significant modification action on PLA film properties and in the other hand their uses for creating active PLA packaging is technically safe.

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