



Incorporation of Waste Orange Peels Extracts into PLA Films

Andrea Bassani^a, Sarah Montes^b, Elena Jubete^b, Jesus Palenzuela^b, Antonio Peñas Sanjuán^c, Giorgia Spigno^{a*}

^a DiSTAS - Department for Sustainable Food Process, Università Cattolica del Sacro Cuore, Piacenza, Italy

^b CIDETEC, Parque Científico y Tecnológico de Gipuzkoa, San Sebastián, Spain

^c Andaltec Centro Tecnológico del Plástico, Martos, Jaén, Spain

giorgia.spigno@unicatt.it

An important and hot-topic field in food packaging is the development of innovative active packaging, based on the incorporation of specific components, such as antioxidant and/or antimicrobial agents, able to modify the internal atmosphere or to be absorbed directly by the food, in order to prolong the product shelf-life. However, due to the increasing concerns of consumers about the plastics and the presence of synthetic chemical compounds in consumer goods, as well as, the importance of increasing environmental sustainability of the materials, has encouraged novel developments. This study is focused on the development of innovative, biodegradable and sustainable PLA-based active packaging solutions with the incorporation of natural antioxidant compounds recovered from agri-food wastes. An antioxidant extract was recovered through hydro-alcoholic extraction from waste orange peels, purified by resin absorption process and formulated as freeze-dried extract or spray-dried with pectin or cyclodextrins as carrier material. These three different formulations were incorporated into PLA films at different concentrations to investigate the influence of extract addition on polymer thermal stability and on colour and mechanical properties of films under accelerated light storage conditions.

1. Introduction

Poly(lactic acid) (PLA) represents the most investigated bio-polyester for a wide range of applications, due to its biodegradability, renewability, good mechanical properties, processability and low cost, even though high brittleness, slow crystallization rate and low barrier properties compared to fossil-based polymers partly limit its applications in food packaging. Nanomaterials, and above all, cellulose nanowhiskers (Arjmandi et al., 2017) and layered silicate clays (Bartel et al., 2017) have been studied for incorporation into PLA to improve mechanical and barrier properties, even though, in the case of food contact, materials migration of nanoparticles should be avoided or, at least, verified (Marinoni et al., 2018). Other authors have investigated the production of PLA nanoparticles loaded with green tea extract for development of innovative food packaging applications (Wrona et al., 2017), such as active packaging. According to European Commission Regulation (450/2009) active materials are defined as “materials that are intended to extend the shelf-life or to maintain or improve the condition of packaged food; they are designed to deliberately incorporate components that would release or absorb substances into or from the packaged food or form the environment surrounding the food”. Our previous research demonstrated that an orange peels extract incorporated into PLA films could be released to food products (Marinoni et al., 2018). Oranges are one of the most important commodities in terms of global agricultural production with 73.33 Mtonnes produced in 2017 in the world (FAOstat). Beyond being consumed fresh, oranges are industrially processed into juice with an estimated world production of 1.61 Mtonnes in 2017 (USDA). After juice production, more than half of the fruit weight is left as residual peels and pulp. This waste has been traditionally valorised as molasses for animal feed, production of pectin, flavonoids and fuel (Lagha-Benamrouche and Madani, 2013). The phenolic compounds and antioxidant activity of orange peels and related extracts have been extensively investigated and demonstrated (Vadivel et al., 2017). As a drawback, natural phenolic extracts are generally very heat and oxygen sensitive, therefore encapsulation strategies can be exploited to increase thermal and oxidative stability of the compounds. This is

Paper Received: 15 April 2018; Revised: 26 August 2018; Accepted: 11 December 2018

Please cite this article as: Bassani A., Montes S., Jubete E., Palenzuela J., Sanjuan A.P., Spigno G., 2019, Incorporation of Waste Orange Peels Extracts Into Pla Films, Chemical Engineering Transactions, 74, 1063-1068 DOI:10.3303/CET1974178

requested in case of direct incorporation of such extracts into a polymeric plastic film before extrusion, since the latter takes place at temperatures above the melting point of the plastic polymer. Spray-drying is one of the most commonly applied encapsulation technologies (Spigno et al., 2013) but it generally requires a carrier to support and encapsulate the bioactive compounds that are to be dried. Polysaccharides are commonly used as carrier materials, including pectin, which can be, on its turn, recovered from orange peels (Tovar et al., 2019), and β -cyclodextrins mainly used to increase solubility and shelf-life of volatiles flavours and fragrances and to stabilize against temperature (Pellicer et al., 2018).

The aim of this research was to develop different antioxidant natural extract formulations starting from waste orange peels for incorporation into PLA before extrusion, checking the influence of extract addition on mechanical and color properties of final films.

2. Materials and Methods

2.1 Waste orange peels extracts

The orange peels extract (OPE) was obtained from waste orange peels (kindly provided by Anecoop S. Coop, Spain), dried at 60 °C until residual moisture < 10% and milled (< 2 mm). Extraction was carried out with aqueous 80 % ethanol at 50 °C, 1 h under stirring, using a 1:10 g:mL solid to solvent ratio (process adapted from Lagha-Benamrouche and Madani, 2013). A crude extract was separated by centrifugation, concentrated 4-fold under vacuum and then purified through an absorption process on an Amberlite resin (IRA-410 from Rohm and Haas, Philadelphia) to remove sugars (fructose, glucose and sucrose), organic acids (citric acid) and minerals (Ca, K, Na, Mg) with a purification process adapted from Scordino et al. (2003). Briefly, resin was initially regenerated with 1 % NaOH, ethanol 96 % and water; loaded with an aqueous dilution of the crude OPE; rinsed with water and then with ethanol 96 % to elute the adsorbed phenolic compounds obtaining the purified extract which was concentrated under vacuum. For freeze-drying, the extract was concentrated under vacuum and reconstituted with water to be frozen and dried for about 72 h by using a Christ Alpha 1-2 LD freeze dryer (during the process, the ice condenser was set at a temperature lower than -50 °C, and the pressure was around 0.120 mbar). For spray-drying, two different carrier materials were tested: β -cyclodextrin (Kleptose, β CD, kindly supplied by Roquette Services Techniques et Laboratoires, France) or citrus pectin (Sigma Chemical, from citrus fruits, with 93.5% galacturonic acid and 9.4% methoxy content). Spray-drying was carried out in a Mini Spray drier (B-290, Buchi, Switzerland) at the following operation conditions: 4 mL/min feeding rate; 667 L/h drying air flow rate; aspirator rate set at 100%; 120 °C inlet air temperature. In the case of pectin use, a ratio of 0.51 of pectin to extract solids was used. Based on the dry matter content, corresponding volumes of concentrated OPE and 2% pectin solution were taken and made up to a final volume of 200 mL with water (final pectin concentration 1%). In the case of β CD, these were added as a water solution 2 % w/v at a solid ratio of 0.75 solid β CD / solid OPE. The obtained freeze-dried and spray-dried powders were analysed for the total phenols content according to the Folin's assay (Vellingiri et al., 2014) expressed as hesperidin equivalents (HE, being hesperidin the main phenolic compound present in the OPE). Thermal stability of the powders was evaluated by differential scanning calorimeter (DSC 1/200 System METTLER TOLEDO) in non-isothermal conditions (scanning from room temperature 30 °C to 380 °C at 5 °C/min, under a 50 mL/min N₂ atmosphere using closed Aluminum standard crucibles). The analysed sample amount was weighted in the range of 6-11 mg in order to have approximately the same amount of total phenols for all the three formulations.

2.2 PLA films

PLA specimens (10 cm*10 cm) were prepared mixing commercial PLA (Hycail HM 1011) with different concentrations (0.25, 0.50, 1.50, 2.0 % wt.) of the different OPE formulations in a Brabender internal mixer (50 cm³ capacity) at 175 °C and then by hot pressing at 175 °C, 100 bar.

The obtained films were analysed for thermal stability by TGA (TGA Q500 of TA Instruments). The samples were then aged in an aging chamber (ATLAS MATERIAL TESTING Suntest XXL+) for 500 h. Colour evolution was monitored after 50, 100, 200, 300 and 500 h measuring the trichromatic coordinates L*, a* and b* (with a colorimeter from Konica Minolta, CM-2600d model) and calculating the total colour difference with Eq(1).

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5} \quad (1)$$

Where Δ refers to the difference of each parameter in comparison with the value measured at time zero.

Mechanical properties of all the films before and after 200 hours were also measured. The mechanical properties (e.g. Young module (MPa), tensile strength (MPa) and elongation at break (%)) were evaluated by tensile tests using a universal testing machine model 3365 (Instron). Rectangular test specimens (65 mm x 4 mm) with a crosshead speed of 50 mm min⁻¹, and an initial gauge length of 40 mm were used.

3. Results and discussion

3.1 Waste Orange peels extracts

Total phenols content of the three different purified OPE formulation resulted: 463.3 mg_{HE}/g, 340 mg_{HE}/g and 370 mg_{HE}/g for the freeze-dried extract, extract spray-dried with pectin and extract spray-dried with β -CD, respectively.

Thermal analysis (Figure 1) showed the freeze-dried sample as the one with the lowest thermal stability, while the sample spray-dried with cyclodextrins, the one with the highest stability. Particularly, the freeze-dried extract started oxidation (increase in curve slope) at 160 °C with a complex series of exothermic phenomena in the range 190 – 280 °C. The sample spray-dried with pectin showed a unique exothermic peak (oxidation) in the range 210 – 270 °C. The sample spray-dried with cyclodextrins showed two minor oxidation phenomena in the range 210 – 230 °C and a big degradation event after 280 °C, probably due to the degradation of the complex formed between extract and cyclodextrins, as suggested by literature (Zhou et al., 2014).

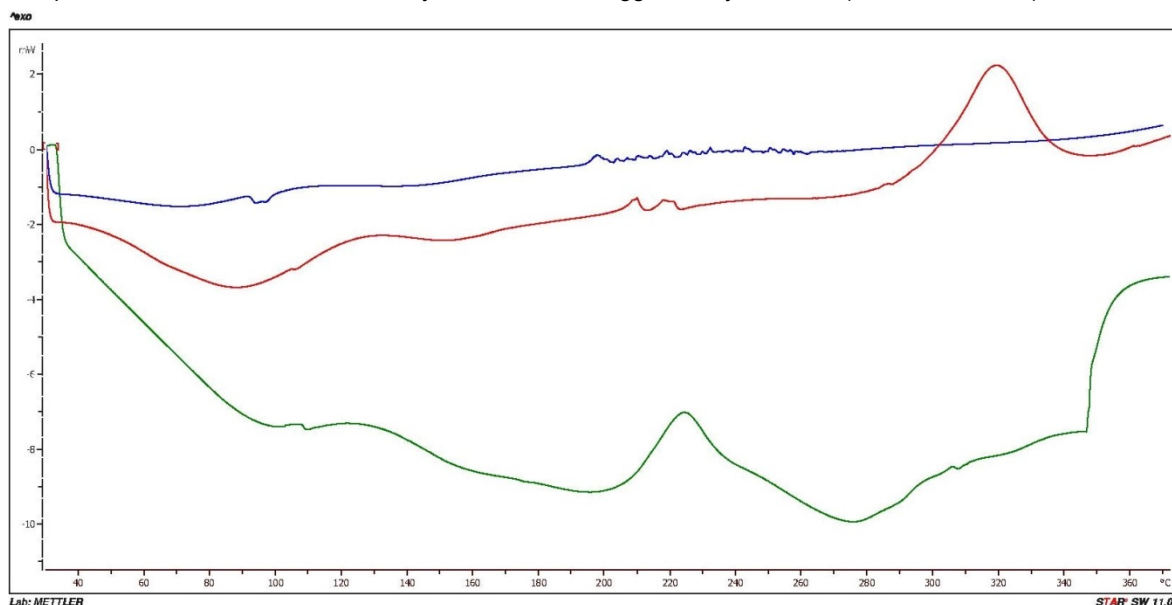


Figure 1: Differential scanning calorimeter scans obtained for samples of purified orange peels extract: freeze-dried (on the top), spray-dried with β -cyclodextrins (in the middle) and spray-dried with pectin (on the bottom).

3.2 PLA films

As partly expected, and as evident from Table 1, addition of OPE, independently on the formulation, conferred to PLA film an orange colour and a 2 % concentration was unacceptable for material processing (as it would also be from the point of view of the cost of the extract additive).

No significant changes in the trends of the degradation temperatures were obtained after thermogravimetric analysis of the different films as shown in Figure 2 for the lowest and highest OPE incorporation level, without any substantial difference due to the extract formulation (freeze-dried or spray-dried).

Based on colour evolution of the enriched PLA (Table 2), as already commented for Table 1, extract addition greatly modified the original colour. Regarding stability during accelerated light exposition, the least stable extract formulation would be the freeze-dried one, while encapsulation with either pectin or cyclodextrins had a positive effect on extract colour stability. Antioxidants release into packed foods depends on the food composition and must be assessed to evaluate enriched PLA as an effective active packaging (Marinoni et al., 2018).

Addition of extracts, in all the three formulations, reduced the values of all the measured mechanical properties compared to the reference neat PLA, with, in most of the cases, an increasing difference for increasing extract concentration (Table 3). Regarding the influence of aging for the same PLA-type, there was a slight tendency to increase in the values of tensile strength and Young's module and a consequent reduction in elongation at break. However, the samples enriched with pectin gave variable results and, as reasonably expected, the freeze-dried extract without carrier addition was the one with the lowest influence on mechanical properties.

Table 1: PLA films obtained through incorporation of orange peels extract formulations.

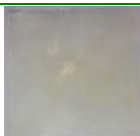
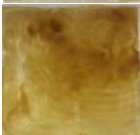
Extract % wt. incorporation	Freeze-dried	Spray-dried with pectin	Spray-dried with β -cyclodextrins
0.25			
0.50			
1.50			
2.00			

Table 2: Colour evolution (ΔE) of PLA films without or with addition of different orange peels extract formulations at different concentrations during aging under light exposition. Standard deviations are not included since ΔE was calculated from mean values of trichromatic coordinates according to Eq(1).

Extract % wt. incorporation	Freeze-dried extract					Spray-dried with pectin					Spray-dried with β -cyclodextrins				
	50	100	200	300	500	50	100	200	300	500	50	100	200	300	500
0	1.7	1.4	2.1	2.6	1.5	1.7	1.4	2.1	2.6	1.5	1.7	1.4	2.1	2.6	1.5
0.25	10.5	10.7	10.2	10.3	10.7	10.5	11.2	13.9	11.5	12.2	11.6	13.5	14.8	15.5	15.6
0.50	15.6	16.5	17.0	15.7	17.2	13.3	14.3	14.6	17.2	18.5	10.6	12.9	15.3	17.6	16.8
1.50	18.9	23.4	27.8	28.4	32.6	16.1	19.9	20.4	22.6	24.1	17.5	20.2	19.8	22.8	24.4
2.00	18.6	23.4	30.7	34.3	37.4	13.0	19.0	22.6	23.5	25.2	17.9	22.8	24.8	29.1	30.9

Table 3: Mechanical properties of PLA films without or with addition of different orange peels extract formulations at different concentrations before and after 200 h aging under light exposition. Results are reported as mean values $\pm$ s.d. NM: not measured.

Sample	Freshly prepared films				Films after 200 h aging		
	Young Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)		Young Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)
PLA reference	3361.61 $\pm$ 188.42	56.82 $\pm$ 4.78	2.21 $\pm$ 0.11		3326.05 $\pm$ 282.25	53.58 $\pm$ 6.37	2.12 $\pm$ 0.40
FD, 0.25	2629.41 $\pm$ 296.38	43.81 $\pm$ 5.38	2.60 $\pm$ 0.62		3092.77 $\pm$ 277.61	53.60 $\pm$ 6.78	2.43 $\pm$ 0.60
FD, 0.50	3176.12 $\pm$ 276.36	54.60 $\pm$ 5.33	2.24 $\pm$ 0.10		3040.31 $\pm$ 327.23	55.23 $\pm$ 6.01	2.61 $\pm$ 0.27
FD, 1.50	3002.64 $\pm$ 148.89	46.46 $\pm$ 3.88	2.00 $\pm$ 0.24		3660.31 $\pm$ 341.02	60.80 $\pm$ 7.67	2.21 $\pm$ 0.19
FD, 2.00	3001.59 $\pm$ 143.81	44.58 $\pm$ 4.61	2.02 $\pm$ 0.24		3062.56 $\pm$ 211.23	34.52 $\pm$ 7.33	1.67 $\pm$ 0.00
Pe, 0.25	3175.43 $\pm$ 194.47	49.37 $\pm$ 4.96	2.01 $\pm$ 0.24		NM	NM	NM
Pe, 0.50	2921.78 $\pm$ 279.28	43.77 $\pm$ 2.93	1.94 $\pm$ 0.12		2864.70 $\pm$ 73.77	45.08	1.88
Pe, 1.50	2463.99 $\pm$ 235.62	36.49 $\pm$ 12.60	2.15 $\pm$ 0.53		162.50 $\pm$ 75.14	8.01 $\pm$ 13.35	2.36 $\pm$ 1.42
Pe, 2.00	3164.45 $\pm$ 161.28	45.72 $\pm$ 0.32	1.77 $\pm$ 0.15		3138.16 $\pm$ 293.18	41.98 $\pm$ 4.94	1.67 $\pm$ 0.00
CD, 0.25	3214.55 $\pm$ 253.43	48.80 $\pm$ 6.71	2.08 $\pm$ 0.17		3140.04	49.70	1.88
CD, 0.50	2789.41 $\pm$ 195.49	45.31 $\pm$ 2.75	2.55 $\pm$ 0.26		3255.55 $\pm$ 538.79	50.78 $\pm$ 9.53	1.91 $\pm$ 0.28
CD, 1.50	3176.57 $\pm$ 228.58	49.79 $\pm$ 2.03	2.36 $\pm$ 0.24		3577.54 $\pm$ 867.02	53.45 $\pm$ 10.97	1.88 $\pm$ 0.00
CD, 2.00	2890.46 $\pm$ 231.05	40.58 $\pm$ 3.84	2.21 $\pm$ 0.46		3325.86 $\pm$ 409.82	51.10 $\pm$ 4.87	1.98 $\pm$ 0.12

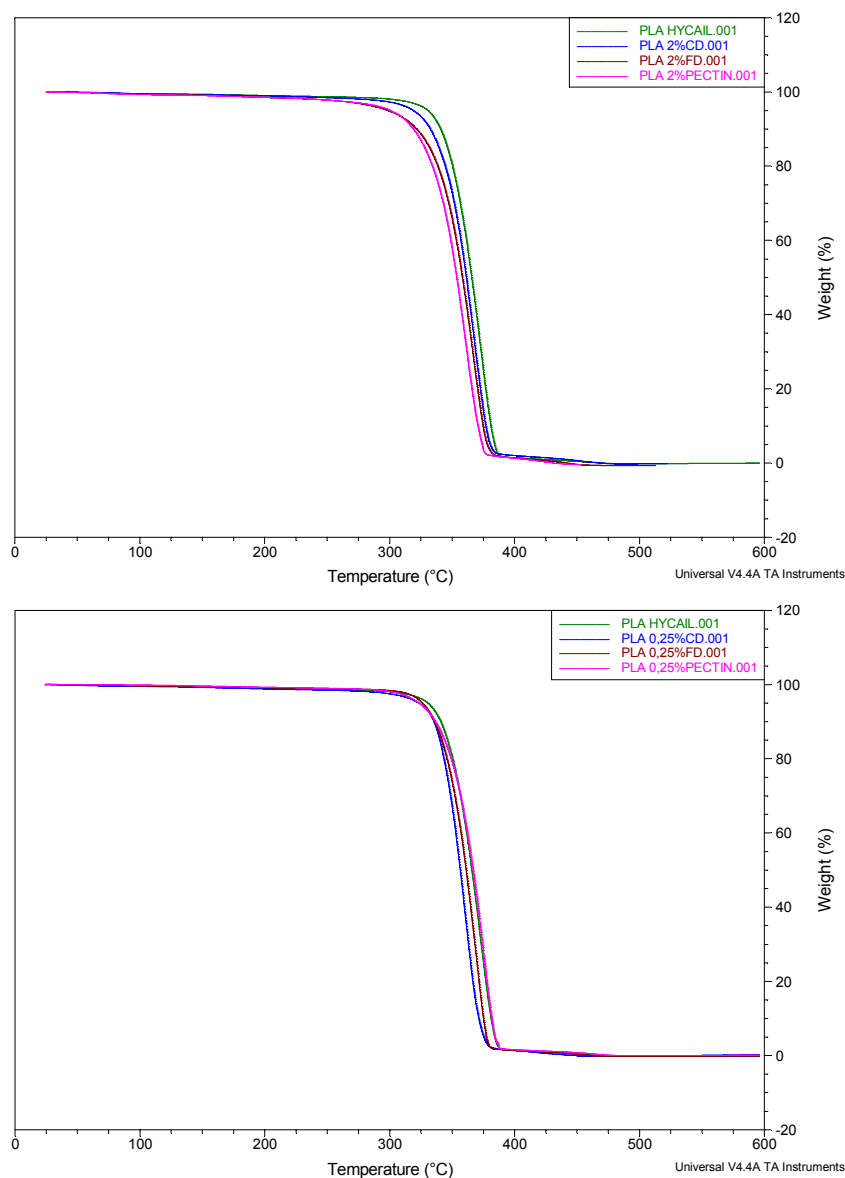


Figure 2: TGA scans of reference PLA film (HYCAIL 0.01) and PLA films added with 0.25% (on the top) and 2% (on the bottom) of different purified orange peels extract formulations: CD (spray-dried with β -cyclodextrins); FD (freeze-dried), PECTIN (spray-dried with pectin).

4. Conclusions

A purified freeze-dried extract with almost 50% content of total phenols was obtained from waste orange peels. Other two different powder formulations were manufactured through spray-drying with citrus pectin or with β -cyclodextrins. Thermal analysis revealed that encapsulation improved thermal stability compared to freeze-drying extract, particularly when cyclodextrins were used, and this is an important aspect if such extracts have to be directly incorporated into plastic films before polymer extrusion.

The three different extract formulations were then mixed at different concentrations, from 0.25 to 2.00 % wt., to commercial PLA and the mixtures were hot pressed to obtain PLA film samples. Extract addition preserved the transparency of the bioplastic but impaired a yellowish colour increasing with addition level and an unacceptable browning at the 2% dosage. Thermogravimetric analysis revealed that any extract formulation, at any concentrations, did not modify the degradation temperature profile of the PLA film. An accelerated light storage test was carried out to identify any effect of extract incorporation on colour and mechanical stability of the material. From the colour point of view, encapsulation could improve the colour stability compared to the directly freeze-dried extract. Mechanical properties (Young module, tensile strength and elongation at break)

were affected by extract addition which led to slightly lower performances and worsening after accelerated light aging, with the freeze-dried formulation leading to the lowest variations.

Acknowledgments

This research was financially supported by the European Union's FP/ research programme under agreement No. 289829 (SusFoFlex project) and the Bio-Based Industries Joint Undertaking under the European Union's Horizon 2020 Research and Innovation programme under grant agreement No 792261 (NewPack project).

References

- Arjmandi R., Suib N., Hassan A., Muhamad I.I., Pa'a N., Zakaria, Z., 2017, Tensile and morphological properties of bacterial cellulose nanowhiskers reinforced polylactic acid nanocomposites, *Chemical Engineering Transactions*, 56, 1327-1332.
- Bartel M., Remde H., Bohn A., Ganster J., 2017, Barrier properties of poly(lactic acid)/cloisite 30B composites and their relation between oxygen permeability and relative humidity, *Journal of Applied Polymer Science*, 17, 44424, 1-10.
- Commission Regulation (EC) No 450/2009 of 29 May 2009 on active and intelligent materials and articles intended to come into contact with food.
- FAOSTAT, Food and agriculture data, <<http://www.fao.org/faostat/en/#home>> accessed 09.04.2019.
- Lagha-Benamrouche S., Madani K., 2013, Phenolic contents and antioxidant activity of orange varieties (*Citrus sinensis* L. and *Citrus aurantium* L.) cultivated in Algeria: Peels and leaves. *Industrial Crops and Production*, 50, 723–730.
- Marinoni L., Montes S., Jubete E., Palenzuela J., Cid G.M., Aguilera D., Spigno G., 2018, Incorporation of nanoclay and orange peels extract into PLA for food applications: migration assessment, *Journal of Applied Packaging Research*, 10, No. 2, Article 5.
- Pellicer J.A., Fortea M.I., Trabal J., Rodríguez-López M.I., Carazo-Díaz C., Gabaldón J.A., Núñez-Delicado E., 2018, Optimization of the microencapsulation of synthetic strawberry flavour with different blends of encapsulating agents using spray drying, *Powder Technology*, 338, 591-598.
- Scordino M., Di Mauro A., Passerini A., Maccarone E., 2003, Adsorption of flavonoids on resins: hesperidin, *Journal of Agricultural and Food Chemistry*, 51, 6998-7004.
- Spigno G., Donsi F., Amendola D., Sessa M., Ferrari G., De Faveri D.M., 2013. Nanoencapsulation systems to improve solubility and antioxidant efficiency of a grape marc extract into hazelnut paste. *Journal of Food Engineering*, 114, 207-214.
- Tovar A.K., Godínez L.A., Espejel F., Ramírez-Zamora R.-M., Robles, I., 2019, Optimization of the integral valorization process for orange peel waste using a design of experiments approach: Production of high-quality pectin and activated carbon, *Waste Management*, 85, 202-213.
- USDA, United States Department of Agriculture, 2017, <<https://www.indexmundi.com/agriculture>> accessed 09.04.2019.
- Vadivel V., Moncalvo A., Dordoni R., Spigno G., 2017, Effects of an acid/alkaline treatment on the release of antioxidants and cellulose from different agro-food wastes, *Waste Management*, 64, 305–314.
- Vellingiri V., Amendola D., Spigno G., 2014, Screening of four different agro-food by-products for the recovery of antioxidants and cellulose, *Chemical Engineering Transactions*, 37, 757-762.
- Wrona M., Cran M.J., Nerín C., Bigger S.W., 2017, Development and characterisation of HPMC films containing PLA nanoparticles loaded with green tea extract for food packaging applications, *Carbohydrate Polymers*, 156, 108-117.
- Zhou S.-Y., Ma S.-X., Cheng H.-L., Yang L.-J., Chen W., Yin Y.-Q., Shi Y.-M., Yang X.-D., 2014, Host-guest interaction between pinocembrin and cyclodextrins: Characterization, solubilization and stability. *Journal of Molecular Structure*, 1058 (1), 81-188.