XXI IMEKO World Congress "Measurement in Research and Industry"
August 30 – September 4, 2015, Prague, Czech Republic

FEASIBILITY STUDY FOR THE DEVELOPMENT OF A *MULTIPARAMETER*-REFERENCE MATERIAL FOR FOOD CONTACT MATERIAL TESTING AND CHARACTERIZATION

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Abstract – This paper reports a feasibility study for the development of a *Multiparameter*-Reference Material (RM) to be employed for food contact material testing and characterization. Two test batches were prepared starting from a film of Poly-Lactic Acid (PLA) and from the same film coated with a silver layer (Ag-PLA) and then they were submitted to optical, morphological, mechanical and chemical characterization. The final objective is to obtain a RM to be certified for chemical composition, to be accompanied by reference values for migration tests (also for evaluating nanoparticle release) and optical and mechanical properties.

Keywords: Reference Materials, food contact materials, packaging, Poly-Lactic Acid, Ag-PLA, migration testing

1. INTRODUCTION

Packaging is an integral part both of the food processing and the whole food supply chain and plays a decisive role in food quality and safety during food product distribution and storage, up to the end use. Food packaging has to perform several tasks, as well as fulfilling many demands and requirements. The current trend is to increase as much as possible food quality, giving priority to consumer demand for high quality and food safety. To adequately respond to an increasingly demanding market, food packaging needs to be more and more performing, active, intelligent and sustainable. Active packaging (AP) is one of the innovative food packaging concepts, that has been introduced as a response to the consumer demand for high quality, safety and extended shelf-life of food products. Current packaging trends include the development of new materials (bio-sourced, nanostructured), new functionalities (antimicrobial, scavengers, control of the atmosphere, etc.) or new technologies. Different materials and methods can be used in order to develop antimicrobial packaging systems.

Poly-Lactic Acid (PLA) has been classified as *Generally Recognized As Safe* (GRAS[1]) and has been approved for use in food packaging (including direct contact applications). The major PLA application today is in packaging (nearly 70%); in recent years it has been developed for a wide range of primary packaging applications (oriented and flexible films, extruded and/or thermoformed packages suitable for common applications). The potential use of the PLA for the active packaging, especially with antimicrobial activity, and the applications of nanomaterials in combination with PLA structures for creating new PLA nanocomposite materials are increasingly studied and an important growth on the development of antimicrobial packaging materials based on PLA polymers is expected in the future, with major focuses on enhancing food quality and safety [1,2].

A key factor related to food safety in packaging is the risk of migration and diffusion of unsafe levels of chemical substances from the contact materials up to the food. Even more so, in the case of active packaging this issue may involve both the package component itself and the additives (incorporated active agents) and becomes even more complex for nanocomposite materials, as it involves all the safety problems related to nanoparticles (NPs).

EU legislation on food contact materials (FCM) is aimed to protect consumer health and remove technical barriers to trade. Under the EU legislation, FCM are regulated by: the Framework Reg. (EC) 1935/2004 on general requirements for all FCM (consolidated version: 2009) [3], the legislation on specific materials and groups of materials, the directives on individual substances or groups of substances, other than the national legislation covering groups of materials and articles for which EU legislation is not yet in place. In particular, Reg. (EU) 10/2011 (consolidate version: 2014)

[1] *Generally Recognized as Safe* (GRAS), FDA - http://www.fda.gov/Food/IngredientsPackagingLabeling/GRAS/
[2] Panel on food contact materials, enzymes, flavourings and

deal with plastic materials and articles intended to come into contact with food [4], and Reg. (EC) 450/2009 deal with active and intelligent materials [5]. In order to ensure food safety, it is stated that FCM must not transfer their components into the foods in unacceptable quantities (migration) and for plastic materials Migration Limits are defined [4]: Overall Migration Limit (OML), Specific Migration Limits (SMLs) for individual authorised substances fixed on the basis of a toxicological evaluation. The regulatory framework on FCM is evolving in order to consider the safety aspects related to the use of new materials, the development and diffusion of active and intelligent packaging and the increasing use of nanotechnologies. Even within EFSA, the need to revise the guidelines produced by the CEF Panel[2] and to develop a *"New Guidance for the safety assessment of a substance to be used in Food Contact Materials"* has been established considering: the availability of new data on food composition and food consumption; the need to alignment with the new EFSA positions and the emerging issues related - as an example - to genotoxicity and nanotoxicity; the need of harmonization with other areas.

The compliance assessment of FCM requires the performing of migration tests following the procedures established by the EU Directives [6,7]. In this context the availability of Reference Materials (RMs) to be employed for FCM testing and characterization, giving reference values on the application of migration tests, could be extremely useful for improving measurement comparability and reliability and promoting standardization.

According to BCR and ISO Guides [8,9], we are conducting a feasibility study for the preparation of a *Multiparameter*-Reference Material (RM) to be employed for food contact material testing and characterization, investigating the possibility to certify the material for the chemical constituents and impurity contents and to provide reference values for migration tests and optical and mechanicals properties. With this purpose, after preparing two small batches of PLA and Ag-PLA test samples, we are submitting them to a morphological, structural, mechanical and chemical characterization, as well as to migration tests and evaluation of NP release. Homogeneity of the test materials was evaluated basing on the raw material production process and, specifically for the Ag-PLA, by observation under the microscope aimed to check the homogeneity of the Ag film deposition.

2. MATERIALS AND METHODS

2.1. Preparation of the test materials

Two test batches, of Poly(lactic acid) PLA and Ag-PLA respectively, were prepared starting from a unique lot of a commercial Poly(lactic acid) PLA Ingeo™ Biopolymer 4043D as pellets supplied by NatureWorks LLC. Film extrusion of PLA was performed in a Haake Rheomex 19/25 QC single screw extruder with a POLYLAB QC drive unit and chill roll system (Karlsruhe, Germany) as shown in Fig.1. During film extrusion of PLA the temperature was 180°C in the feeding zone and in the die. The material was extruded with a screw speed of 30 rpm and the temperature of the water entering the chill roll was 40°C. The PLA film thickness was about 100 μm. The final dimensions of the tests samples were 3 x 6 cm^2.

Fig. 1. Experimental set up for film extrusion

The test batch of Ag-PLA was obtained by coating the same PLA film with Ag layer deposited by RF sputtering technique [10]. The Ag coating was deposited starting from a silver target (99.99 % purity) at RF power of 40 W in Ar atmosphere (99.9999 % purity) at a pressure of 1.6 Pa.

Final dimensions of the tests samples were (equally to the first batch) 3 x 6 cm^2. The two different types of test samples are shown in Fig. 2. From both batches, test samples were then picked up in order to perform all the scheduled tests.

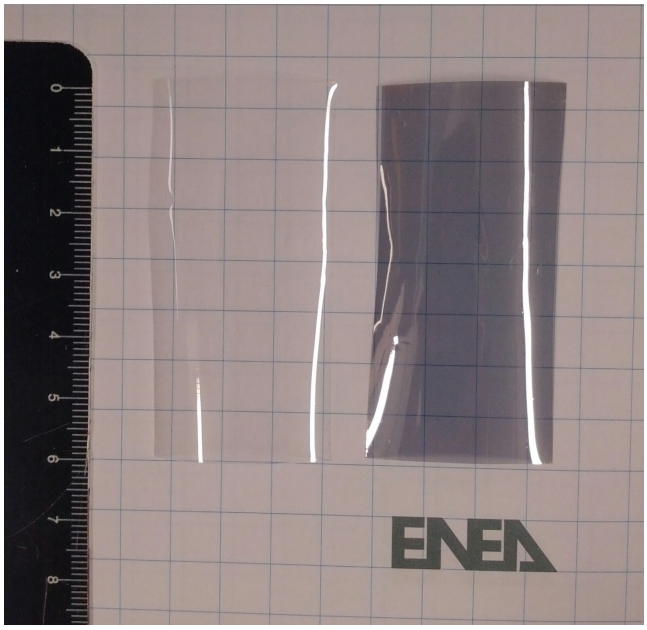

Fig. 2. Test samples of PLA (left) and Ag-PLA (right) 3 x 6 cm^2 films

[2] Panel on food contact materials, enzymes, flavourings and processing aids - http://www.efsa.europa.eu/en/panels/fip.htm

2.2. Characterization of the test samples

Morphological characterization, performed by Scanning Electron Microscopy SEM/FEG, showed a uniform coverage of the PLA surface with the Ag coating. Optical transmission was investigated by an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. The spectra of both the uncoated PLA film and the Ag-PLA sample are shown in Fig. 3. The measurements revealed a transmission of about 90% in the visible range for the uncoated PLA sample and of around 55-70% for the Ag-PLA sample, thus ensuring a sufficient inspection inside the package.

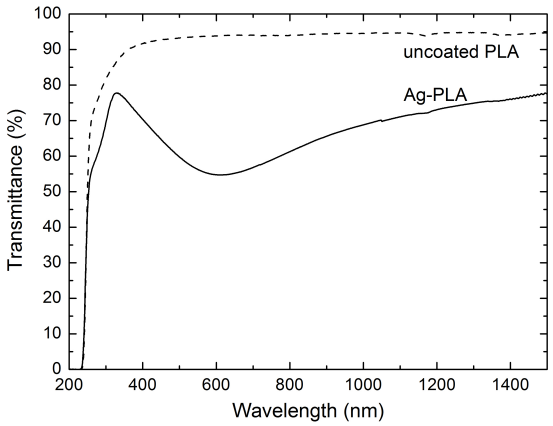

Fig. 3. Optical transmission spectra of the uncoated PLA film and the Ag-coated PLA sample.

For tensile tests a total of five specimens were prepared by cutting rectangular samples from extruded films before and after coating deposition in the longitudinal direction of film extrusion. The test specimens were placed in a conditioning room at 24 °C and 50% relative humidity for 24 hours. Specimens measuring 20 mm in initial length, 15 mm in width with a thickness of about 0.06 mm were tested. Samples were then subjected to tensile testing according to ASTM D 882 using a MTS Alliance RT 50 tensile tester equipped with a 2 kN load cell and flats grip and the average of results was considered. The experiments were conducted at the deformation rate of 2.0 mm/min. The mechanical properties of PLA film and PLA film with Ag layer deposited by sputtering technique (PLA-Ag) were evaluated from stress-strain curves (not shown) and the principal mechanical parameters are reported in Table I.

Sample	E (MPa)	σ_b (MPa)	ε_b (mm/mm)	Stress max (Mpa)
PLA	2986 ± 133	46.6 ± 2.6	0.082 ± 0.02	51.5 ± 2.3
PLA-Ag	3116 ± 200	51.6 ± 1.6	0.063 ± 0.01	58.5 ± 2.6

Table I. Mechanical parameters extracted from the stress–strain curves. (E: elastic modulus; σ_b: stress at break; ε_b: deformation at break).

Elastic modulus, stress at break, strain at break and stress max of the pristine PLA film are slightly improved in the PLA-Ag film. As matter of fact both the sputtering conditions used for the Ag deposition and the coating of the Ag layer on PLA surface did not change significantly the mechanical properties of the extruded polymer.

Migration tests were performed as stated from the current regulation [6,7], considering both global and specific migration. The following simulants were employed: ethanol 10% (V/V) in aqueous solution (simulant A), acetic acid 3% (w/V) in aqueous solution (simulant B), sunflower oil (simulant D2). In particular, test samples of PLA and Ag-PLA were divided in two aliquots with dimensions 3 x 3 cm^2 and put in contact with 22.5 ml of each simulant, so to have a surface/Volume ratio of 2.5. The tests were carried out at different temperatures (T = 20 °C, T = 40 °C, T = 70 °C) using a water thermostatic bath NUVE BS402. The tests at T = 20 °C and T = 40 °C lasted for 10 days and global migration was evaluated determining the sample weight losses at the end of the test, while the solutions for specific migration evaluation were picked up at the following times: 5 min, 30 min, 1 h, 2 h, 4 h, 6 h, 24 h, 3 days, 10 days. The test at T = 70 °C lasted for 2 h and global migration was evaluated determining the sample weight losses at the end of the test, while the solutions for specific migration evaluation were picked up at the following times: 5 min, 30 min, 1 h, 2 h. All tests were performed at least in duplicate. The solutions obtained from the migration tests will be analysed for elemental composition in order to evaluate also the leaching capability for trace elements.

Furthermore the elemental contents of the two test batches, and in particular the total Ag content of Ag-PLA, will be determined. For this purposes the procedure for sample complete dissolution by a Microwave High Pressure Digestion System MILESTONE MLS 1200 MEGA was set up (Maximum Power = 650 W, free pressure rise). Different reagent mixtures were tested in order to define the better conditions for obtaining a total dissolution of different sample amounts (from about 0.050 g up to 0.250 g). The use of different reagents, in different volumes, was investigated: concentrated HNO_3 (69.9%v/v), V = 3 ÷ 6 ml; 2 ml of concentrated HNO_3 (69.9%v/v) + 1 ml of concentrated H_2O_2 (30%v/v). The obtained solutions were filled up to the 25 ml final volume with high-purity water (resistivity > 18 MΩ) in glass flasks.

Elemental analysis will be performed by Inductively Coupled Plasma Atomic Emission Spectrometry Analysis (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry Analysis (ICP-MS). For ICP-AES analysis, a Varian VISTA MPX (Axial Configuration; 1.2 kW; Ar 15 l/min; simultaneous 1.12 Mpixel CCD detector) will be used. ICP-MS analysis will be performed by a Bruker Aurora M90 (90 degree ion mirror ion optics; Collision Reaction Interface). The ICP-MS will be also interfaced with a Field Flow Fractionation system (Postnova AF2000 MultiFlow equipped with UV/VIS PN3212 detector), for a sensitive and selective detection and characterization of NPs.

ACKNOWLEDGMENTS

The work presented in this paper has been carried out with the financial support of the Italian Ministry of Research, in the framework of the Agri-food National

Cluster (CL.A.N.) project *"SAFE&SMART - New enabling technologies for food safety and food chain integrity within a global scenario"* (sept 2013-2016).

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