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RESEARCH ARTICLE

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INTRODUCTION

The transparent barrier flexible packaging market is growing worldwide at a rate of 10 to 15% per year [1]. The use of vacuum deposition techniques to produce transparent barrier layers such as aluminium oxide (AlOx) or silicon oxide, has become a favourable and powerful tool, even if ethylene vinyl alcohol copolymer co-extruded barrier layer films, polyvinylidene chloride coated films [2] and polypropylene film [3] are traditionally the most used materials to produce food packaging. Surface treatments are recognized as one of the most efficient solution to modify commercial polymer film surfaces. The control of topography and chemical composition of film are key parameters to define the efficiency of each method. To be used in a large-scale manufacturing, these processes have to be very cheap and safe. From this point of view, a suitable solution could be the fluorination [4, 5] or the use of plasma [6, 7]. There are a lot of applications for rigid packaging (e.g. boxes, easy open lids for the storage of products containing meat and fish, deep drawing capsules for the closure of liquor, wine, oils etc.) or semi-rigid packaging (such as trays to contain jams, stewed fruit or milk-based dessert). They are produced applying a coating on aluminium surface, previously degreased and treated with chemical conversion processes. They allow applying the coating and to offset printing on plain sheets; then it can be deformed by deep drawing, without any detachment of the polymeric coating from the laminate. Furthermore, the pre-treatment of the surface confers an optimal adhesion of the polymer to the support

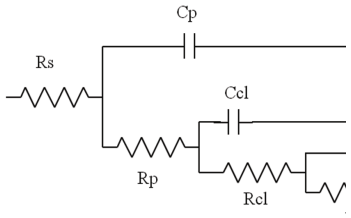
(which allows overcoming even the subsequent processes of pasteurization and sterilization), leading to a greater protection from corrosion. The development of the chemicals used in the pre-treatment of metal surfaces has recently evolved very much. In fact they moved from rinse treatments which include immersion of the laminates in baths and subsequent washing in demineralised water, to no rinse treatments that involves the application of products on metal by using various systems (roller or spray) and that do not require any subsequent washing of the surfaces. The Laminazione Sottile group has a longer experience in the surface treatments process on rigid and semi-rigid packaging and think to develop similar process for flexible packaging. To perform these treatments, the laminate should be subjected to at least one thermal degreasing to eliminate the residues of lubricants used in the rolling and provides a degree of wettability AB according to UNI EN 546-4. Electrochemical tests are used to "measure" and numerically present the corrosion resistance of the coated products in contact with the testing solutions: saline or acetic saline solution. In addition, "technological" tests have been performed, such as pasteurization, neutral sterilization, alkaline sterilization and LAS sterilization (in a solution of lactic/acid/Acetic/Saline when the conservation of acid and/or salted food has to be tested) [8].

MATERIALS AND METHODS

The material examined in this work is a laminate of annealed aluminium alloy EN AW 8079 with a thickness of 37 μm, commonly used for lids for sealing yogurt cups. Used aluminium was then lacquered by applying an universal thermoplastic heat-sealing lacquer PVC free 5.5g/m^2 dry film, used to heat-seal the lid on the cups in polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC), some types of polyethylene (PE) and polyester (PET). This kind of lacquer is directly in contact with the yogurt. The aim of present paper is to compare, in terms of adhesion of the heat-sealable coating and of corrosion resistance, a thermal degreased standard laminate to a laminate after the application of a chemical conversion coating Zirconium based (absolutely Chromium free [9]), with an applied weights of 2.5 and 4.5 mg/m^2 of Zirconium. The amount of Zirconium to be used to pre-treat the surface is determined by analyzing Plasma spectrometry emission (I.C.P. Inductively Coupled Plasma) of the acid dissolution on the surface of aluminium. Potentiodynamic polarization measurements (DC) have been performed to evaluate corrosion resistance of untreated and pre-treated aluminium. Tests were carried out according to ASTM G3 and G5, by using a three electrode cell: specimen as working electrode (WE), platinum as counter electrode (CE) and a Saturated Calomel Electrode as reference (Ref SCE) in a NaCl 3.5%w solution in aerated condition at ambient temperature. The Open Circuit Potential (OCP) was recorded for 1 hour before performing DC test with a scan of the potential that highlighted the cathodic and the anodic range. From the experimental polarization curves the corrosion current density, icorr, the passivation current, i_{pass} and the corrosion, E_{corr} and pitting E_{pit} potentials were obtained. icorr values were estimated by extrapolating the linear region of the anodic potentiodynamic response to the corrosion potential. The potentiodynamic measurements are a powerful tool for evaluating electrochemical phenomena that occur on metallic surfaces. Moreover, they can be an indirect measurement of protective action, of any conversion layers obtained using pre-treatment carried out upstream of the coating process [10, 11]. The evaluation of the corrosion resistance of coated aluminium has been carried out with the Electrochemical Impedance Spectroscopy (EIS) measures. This AC measurement was performed in a frequency range between 10^5 and 10^{-2} Hz. The results are shown as a Diagram of Bode. EIS tests were carried out on the varnished laminate

in a NaCl 3.5%w solution acidified with lactic acid to pH=4.0, simulating the aggression produced by some aliments such as yogurt or small cheese portion. With EIS it can be obtained information about defects in the organic coating, the evolution of the corrosion phenomenon and functionality of the conversion layer. The metal substrate-conversion layer-polymeric resin system can be correlated to an equivalent electric circuit, where each interface is associated with a parallel RC as shown in Fig.1.

Fig. 1. Equivalent electric circuit associated with untreated metal-conversion layer-polymeric resin system.



Referring to Fig.1, Rs is the resistance of the solution, Rp-Cp is the resin/solution interface, Ccl-Rcl is the resin-pre-treatment interface and Cdl-Rdl is the pre-treatment-metal interface.

It is possible to associate a constant of time to each of the three RC parallel: the time constant T1 relative to the parallel Rp-Cp, the time constant T2 relative to the parallel Ccl-Rcl, and the time constant T3 relative to the parallel Cdl-Rdl, at high, intermediate and low frequencies, respectively. These time constants correspond, in the diagram of the impedance modulus to a gradient variation, and in the diagram of the phase angle to a change of curvature. The adhesion of the coating has been evaluated by performing Cathodic delamination measures by scratching a restricted area of the coating, leaving the metal substrate to a direct exposition to electrolyte, leading to detachment of the surrounding polymeric film due to the reduction of metal surface (specimens work as cathode under an applied constant negative voltage). Data have been depicted in diagrams representing current trend as a function of the exposure time, and it is possible to obtain information about the trend of the delamination phenomenon over time. At the end, after the sample are washed and dried, a peeling test is performed. From the measurement of the area of exposed metal it is possible to discover the advancing speed of the delamination.

RESULTS

Fig.2 shows potentiodynamic polarization tests results performed, reported as OCP Potential vs. concentration of Zr, comparing the standard annealed material (350°C for 5h) and the same material after chemical surface treatment in Zirconium no rinse [12], (two different concentration of Zr). Results highlight an increase of the value of Ecorr in a zirconium pre-treatment and a further increase of Ecorr value is shown when the zirconium concentration increases.

Fig. 2. Ecorr of potentiodynamic polarization curves performed on thermally bare annealed material and the same material after surface pre-treatment with Zr to 2.5 mg/m² and 4.5mg/m²

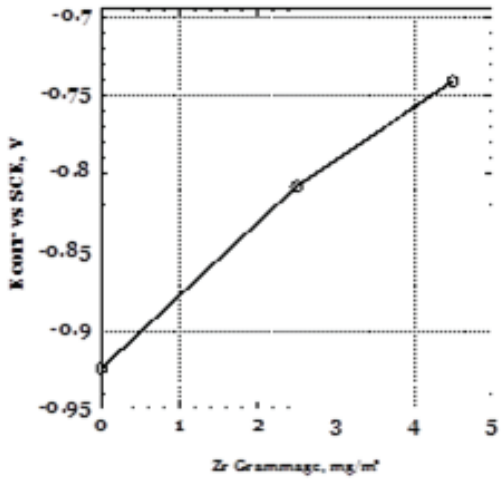


Fig.3 shows the performance of the EIS measures on specimens subjected only to thermal degreasing. At low frequency, it is measured an impedance initial equal to approximately $10^{10}\Omega$cm2, after a day decreases by two orders of magnitude (about $10^{8}\Omega$cm2), after 7 days is reduced to about $10^{6}\Omega$cm2 manifesting a reduction of almost 4 orders of magnitude. Fig. 4 shows the trend of the EIS measures on specimens subjected to treatment with zirconium at low concentration. Initially, it is observed a value of the impedance at low frequencies on the order of $10^{11}\Omega$cm2, while it is reduced to about $10^{10}\Omega$cm2 and to $10^{9}\Omega$cm2 after 1 and 7 days of exposure, respectively. The behaviour of the specimens after treatment with zirconium at high concentration is shown in Fig.5. Initially, the value of the impedance at low frequencies is approximately $10^{9}\Omega$cm2 and tends to be reduced after 7 days to about $10^{8}\Omega$cm2. Comparing the EIS results, one observes a higher performance of the specimens subjected to treatment with zirconium, using a low concentration of Zr is obtained the coating that provides the most effective protection. The cathodic disbondig test presents the measures reported in

Fig. 3. Bode plot in aerated solution of NaCl3.5%w acidized to pH 4 with lactic acid on aluminium laminate varnished with 5.5g/m² of thermo sealing lacquer only thermally degreased.

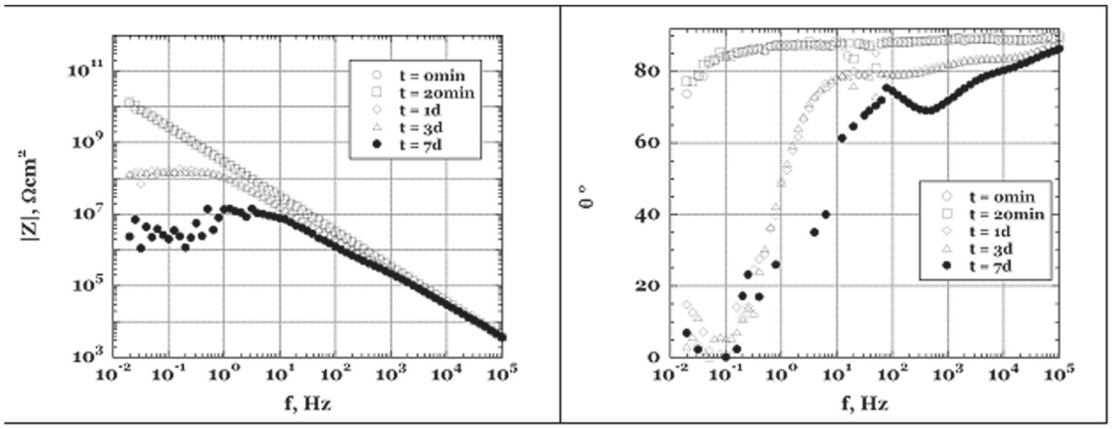


Fig. 4. Bode plot and phase angle in aerated solution of NaCl 3.5%w acidized to pH 4 with lactic acid on aluminium laminate with 5.5g/m2 of thermo sealing lacquer and pre-treated with Zr 2.5 mg/m2.

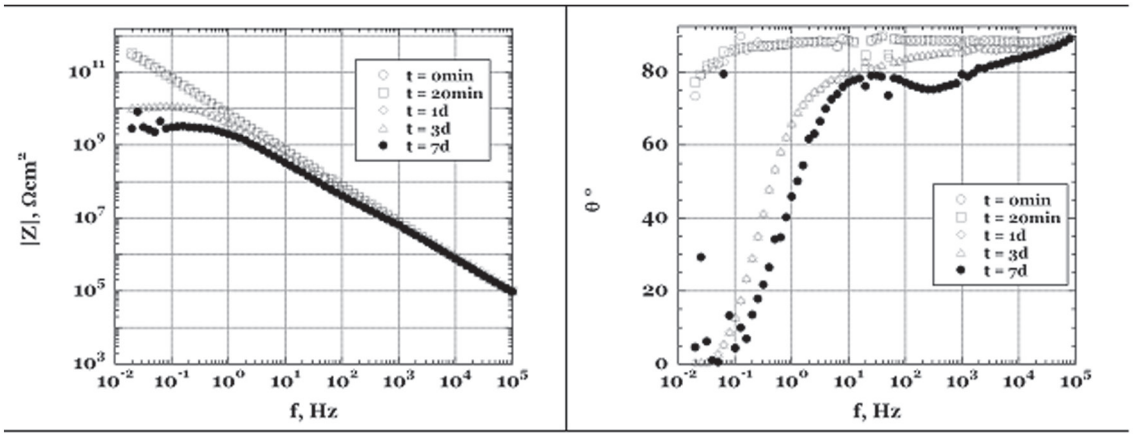


Fig. 5. Bode plot and phase angle in aerated solution of NaCl 3.5%w acidized to pH 4 with lactic acid on aluminium laminate with 5.5g/m2 of thermo sealing lacquer and pre-treated with Zr 4.5 mg/m2 and varnished.

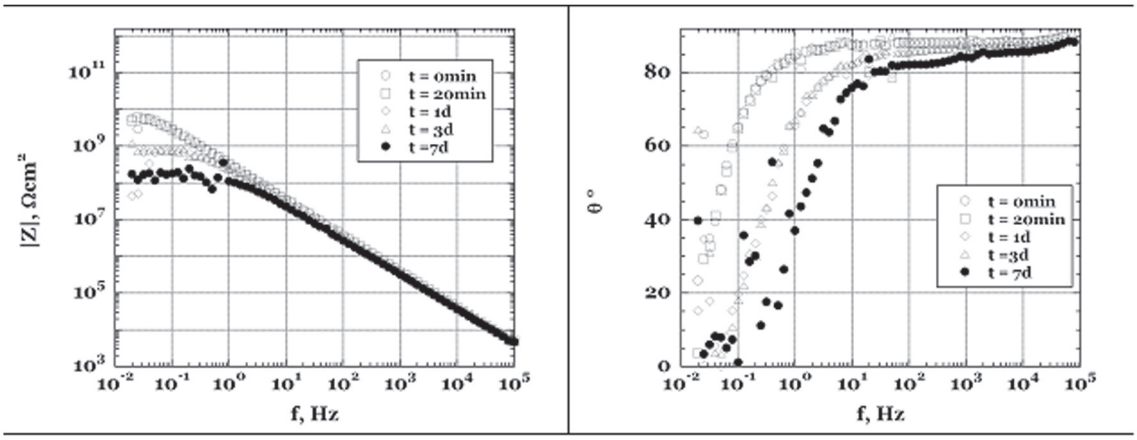


Fig. 6. Trend of the current as a function of the time in a cathodic delamination test conducted in a solution at 0.3M of sodium sulphate on aluminium laminate with 5.5g/m2 of thermo sealing lacquered.

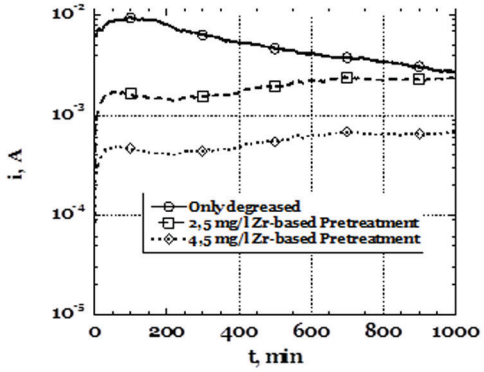


Fig.7. Samples as they appear after the test of cathodic delamination. Left sample of varnished aluminium only thermally degreased, right sample varnished and pre-treated with Zr 4.5 mg/m2.

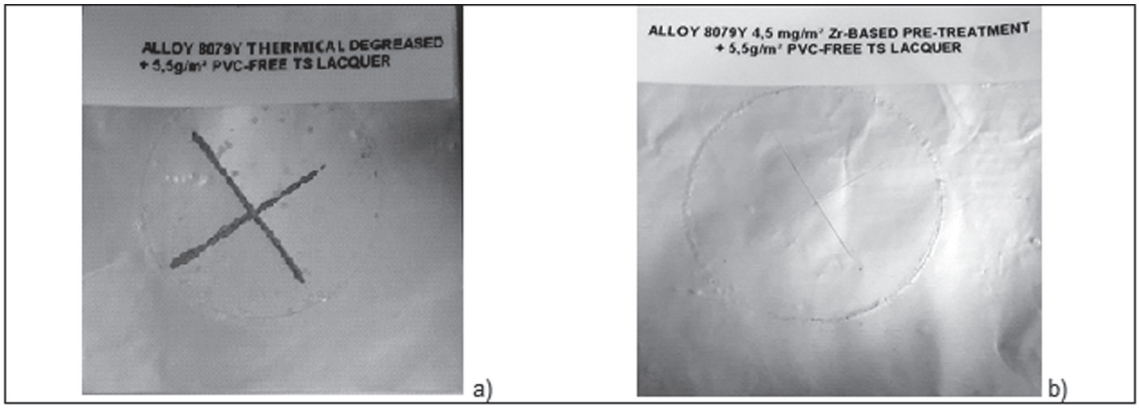


Fig 8. SEM of the sample observed after the cathodic delamination test. a) varnished aluminium only thermally degreased, b) varnished aluminium pre-treated with Zr 4.5 mg/m2.

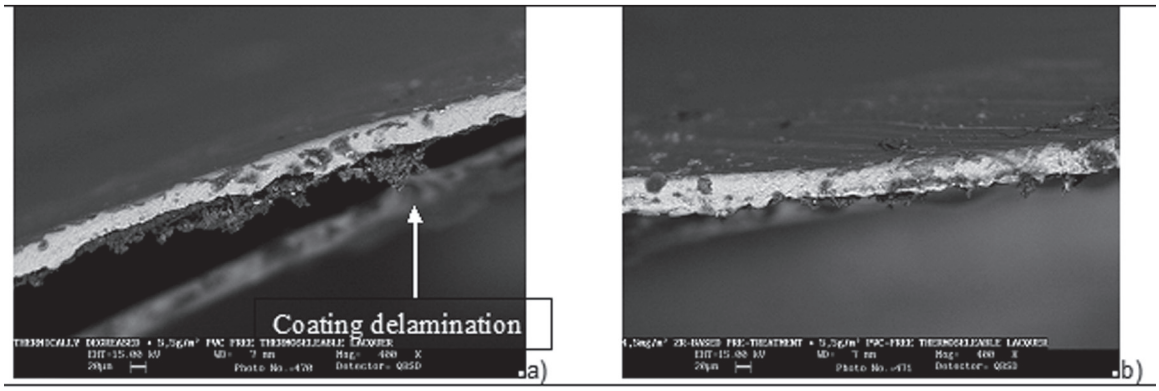


Fig.6, test carried out on Zr pre-treated specimens highlight low values of current respect the specimens with only thermal degreasing. Fig.7a shows the thermal degreased specimens with a small disbonding around the cross, and Fig.7b show the Zr pre-treated specimen without any mark of disbanding around the cross. An evidence of disbonding is shown in Fig.8a with the image acquired at SEM, on the specimens with only thermal degreasing. Fig.8b show a specimen pre-treated with Zr 4.5 mg/m^2, no delamination is visible.

3 CONCLUSIONS

From dc and ac data reported in this paper it has been observed a greater resistance of the specimens subjected to chemical pre-treatment with the zirconium compared to the simple thermal treatment materials (usually adopted in flexible packaging). Further confirmation came from measurements of cathodic disbonding and the metallographic observations. Furthermore, it was found that it is appropriate to operate with a low concentration of zirconium to maximize the corrosion resistance of the coating.

The chemical conversion treatments on the surface of aluminium laminate (and its alloys) of micrometric thickness made possible by the "no rinse" treatments, open up new horizons in the world of flexible packaging. It is possible to increase, the corrosion resistance and the adhesion of polymer coatings (coatings, adhesives, inks) achieving qualitative standards which have been unimaginable until today. The sectors that will get the most benefit from these treatments are those where the packaging has to undergo severe mechanical deformation or in the packaging of products that are particularly aggressive and corrosive. The electrochemical tests prove to be adequate to the needs and allow, in a short time and with precision, the evaluation of: (i) the corrosion resistance of the manufactured articles, and (ii) the adhesion of polymer coatings on metal offering evaluation tools usable not only in the design stage and approval of products, but also in the phase of standardization and verification of the process. Finally, the advantages and disadvantages related to rinse and no rinse treatments have been summarized in Table 1.

Table 1. Advantages and disadvantages of rinse and no rinse treatments

Rinse		No Rinse	
Advantages	Disadvantages	Advantages	Disadvantages
With immersion, the surface are certainly wet	High costs of the installation and management	Low cost of plant and maintenance	Not easy product application
On the two sides of the sheet the metal treatment is homogeneous and uniform	Plant that take up much space	Plant is very compact	Risks of not perfect and constant weight of the product applied
Fast process, typical >200m/min	Large volumes of reagents into the tanks	No cost of wastewater treatment: reagents completely consumed	Low speed process, typical <120m/min
	Need for water treatment and wastewater	Low volumes of pretreatment reagents	
	Costs for wastewater treatment and sludge disposal	It's easy to change product pretreatment	
	Waste of product for the "over flow		

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