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Surface and Microstructural Failures of PET-Coated ECCS Plates by Salmon-Polymer Interaction

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Abstract: The new types of knowledge-intensive, multilayer containers consist of steel plates protected against corrosion by nanometric electrolytic chromium (Cr^0) and chromium oxide (Cr_2O_3) layers chemically bonded to polyethylene terephthalate (PET) polymer coating to preserve food. It was observed that after emptying the cans, the salmon adhered to the polymer coating, changing its color, and that this adhesion increased with longer storage times. This work was aimed at determining the product-container interactions and their characterization by X-ray diffraction (XRD), confocal Raman and micro-Raman imaging and scanning electron microscopy (SEM) analysis. The zones of adhesion showed surface changes, variations in crystallinity and microstructural degradation of the PET coating. In addition, localized damages altering the functional properties of the multilayer system were observed as microcracking in the chromium layers that protect the steel. The degradation undergone was evaluated and characterized at a surface and microstructural level to establish the failure mechanisms, which were mainly associated with the activity of the adhered muscle and its biochemical components. Finally, a recommendation is done to preserve the useful life and functionality of cans for the preservation and efficient use of resources with an impact on recycling and environmental conservancy.

Keywords: salmon; packaging; metal-polymer; layers; failure diagnostics; characterization

1. Introduction

Quality control in the production of canned fish is focused on the processes oriented to produce and preserve a uniform and acceptable product after storage in order to meet and comply with high standards, traceability and food safety conditions [1].

In a supermarket where fish are offered in attractive and ready-to-cook units, color is one of the major attributes that affects the consumer perception of quality [2]. Visual appearance is often the only criterion on which the consumer has to base his or her selection of fish purchase.

However, the quality of materials does not always follow such rigorous standards concerning environmental sustainability, and their life cycle rather becomes the responsibility of suppliers.

Selecting adequate, eco-efficient food containers with a good recycling performance is a key factor that plays a major role in environmental preservation, especially considering the large number of containers produced worldwide [3]. Remarkable achievements for recycled PET (polyethylene terephthalate) can be found in several fields of application, such as medical vascular prostheses, agricultural textile films, hydrophobic membranes, traffic signs and paper bins, among others [4].

The material employed in this study has been designed for use in salmon containers and consisted of a metal-polymer composite made up of a multilayer no more than 200 microns in total thickness.

The observations made in earlier studies have determined that a small percentage of salmon muscle adheres to the interior surface of container walls. Furthermore, these analyses have evaluated the mechanism of adhesion between the salmon muscle and the protective polymer, the influence of the degree of salmon freshness and the effect of the polymer surface failures on adhesion [5]. From the research line above, the present work intends to determine the effects on the base steel-chromium layer interface and the changes in the multilayer container system; these being knowledge-intensive differentiating aspects, validated through a set of material characterization techniques.

PET coatings provide an improved protection barrier effect between the food and chromium layers deposited on the base steel of the container. The layers and metal substrate combine together to give abrasion and degradation resistance against aggressive electrolytes and structural rigidity to the can. The PET polymer is located in the internal wall of the container and contributes to preserving the organoleptic characteristics of food in time, preventing physicochemical interactions with the environment.

However, multilayer composites have complex behaviors, showing failures involving delamination, contamination and chemical degradation [6]. Our hypothesis states that the adhesion of biopolymers or amino acids of food cans affects the polymer coating and the metal substrates in time and is an additional problem that can also decrease the performance of composites with regard to their functionality as a container.

Furthermore, an important aspect in salmon packaging is the production of energy in the postmortem muscle, where the oxygen supply to the muscle tissue is interrupted, and then, the energy production is restricted. Postmortem glycolysis results in the buildup of lactic acid in fish exposed to the stress of transport and/or slaughtering with the concomitant decrease in muscular pH in time [7].

The manufacturing processes to ensure sufficient shelf-life of canned foods include heat-treating by steam, steam-air mixtures, water or spraying water. The amount of heating needed in the coldest spot, used as a reference point to prevent food spoilage and the presence of viable microorganisms, is regularly in the range 4–12 min at 121 °C for some typical canned food products [8–10]. However, quality controls have detected the occurrence of food adhesion to the polymer-coated can walls arising from the application of these heat treatments; such adhesion has been linked to chemical bonding factors at the polymer interface level. It has been reported that proteins are the major cause of this adhesion [11]. Proteins are large biological molecules consisting of chains of covalently-bound amino acids. The bonds formed between the amino acid residues can be of any of these four types: covalent, electrostatic, hydrogen and hydrophobic [12].

A series of physicochemical processes occur inside the container during storage, inducing changes that affect the freshness of canned fish, and therefore, both the canning production processes and technologies play an important role in prolonging the useful life of end-user applications made up of composite materials [8,13,14]. The chemical changes affecting the industrial molecules are strongly related to the crystallinity of polymers and occur especially with the sterilization temperatures employed in the canning processes; thus, extreme environmental conditions may degrade PET coatings [15,16] and expose the underlying metal substrates.

This study is intended to determine the salmon-PET polymer interactions, to evaluate the effects on multilayers, to characterize the degradation or failures resulting from the adhesion of salmon muscle to the polymer coating surface and to assess the microstructural changes undergone, correlating all results through low-dimension techniques to estimate the impact on the container's functionality that may limit its useful life and its recycling capacity.

The damage in localized points of the polymer surface by the physicochemical adhesion of salmon muscle to the can wall is increased by the manufacturing defects of the container, reaching the

multilayers and producing partial morphological and structural degradation, which are key aspects in quality control systems.

Failure analysis work on food containers is worthy both to consumers and manufacturers to preserve the environment and for recycling purposes, respectively.

2. Materials and Methods

The material employed in this study is an eco-efficient, environmentally-friendly, chromium (VI)-free (non-carcinogenic) metal-polymer. This thin, multilayered electrolytic chromium-coated steel (ECCS) laminate protected by a polyethylene terephthalate (PET) coating is employed in the salmon canning industry. The food container employed in this study was manufactured in one of the main canning factories in Chile, a country whose aquaculture industry has grown to become the second largest producer of salmon commercialized worldwide. The chemical composition of steel employed in the manufacturing of food cans for this work consisted of 0.074% C, 0.260% Mn, 0.021% P, 0.016% S, 0.012% Si, 0.032% Al, 45 ppm N and Fe (remaining percentage).

The steel laminate was protected by a coating generated by electrolytic deposition and consists of 0.01 μm-thick chromium Cr^0 and chromium oxide Cr_2O_3 with an average thickness of 0.01 μm and a total chromium content of 101.33 mg/m^2. This electrolytic chromium-coated steel (ECCS) plate had a 30 μm-thick layer of polyethylene terephthalate (PET) consisting of polymerized units of dimethyl terephthalate and ethylene glycol, applied on the surface as a protective barrier against the canned food content. The biaxial-structure PET polymer coating was applied as a film bath on the ECCS sheet.

The metal-polymer salmon cans were manufactured employing 50 mL of a 2.5% NaCl solution, sterilized at 120 °C for 60 min, immersed in a warm water bath in the range of 50–80 °C prior to sterilization. The containers under study were stored for different time spans from 1 week to 14 months at 20 °C before opening. The experimental study evaluated salmon adhesion in those cans stored for 14 months; the average percentage of adhesion for the samples analyzed was 2.5%–3.5% of the total weight after complete emptying of the can in the laboratory (Figure 1).

Figure 1. Muscle residues adhered to PET polymer after emptying the container. Areas of polymer coating with and without salmon adhesion.

Later, the removal of salmon muscle adhered to the can walls was performed with 6 mol/L urea solution to form hydrogen bonds and unfold the proteins. The most representative cans, concerning the areas of salmon adhesion and stored for a period ranging between 12 and 14 months, were selected. The effects of urea and the changes on the multilayers were evaluated and characterized in the areas of the greatest concentration of failures or evident morphological changes on the polymer surface.

The metal-polymer substrate was characterized by X-ray diffraction (XRD) with a D2 Phaser diffractometer (Bruker Corporation, Bruker, Germany). The equipment employs Ni-filtered Cu radiation (30 kV and 10 mA), a 1-mm anti-scatter slit, a 2.5° Soller slit and a LYNXEYE™ detector. The alignment is regularly checked against the NIST Standard Reference Materials (SRM) 1976 alumina plate standard. Patterns were collected in the 5–70° range, counting 5 s per steps of 0.01°.

The surface characterization of salmon adhesion on the PET polymer was carried out by SEM using a LEO 400 series scanning electron microscope (Zeiss, Jena, Germany) and confocal Raman imaging with a spectral resolution at 532 nm to determine the distribution of the different components on the sample.

All Raman images and spectra were recorded using an alpha 300 RA confocal microscope (Zeiss, Jena, Germany) equipped with a CCD camera, an Ultrahigh Throughput Spectrometer (UHTS), frequency-doubled Nd (YAG laser used for 532 nm excitation) and a Zeiss 100× air objective (Numerical Aperture = 0.9). The camera and spectrometer parameters are listed below; CCD Camera DU970_UVB; spectrometer UHTS300; the measurements were acquired using the WITec Control FOUR software (WITec, Jena, Germany) and analyzed with the WITec Project FOUR (WITec, Jena, Germany) and the WITec Project FOUR Plus software (WITec, Jena, Germany), respectively. Points in the directions *X*–*Y* and *X*–*Z* evidencing color changes in the samples were analyzed.

The multilayer composite samples were analyzed by micro-Raman spectroscopy (B&W Tek Inc., Newark, NY, USA). The equipment employed to provide information on the samples consisted of two back-illuminated fiber-coupled spectrometers featuring 633-nm and 785-nm wavelengths. The experimental procedure of this technique considered mainly the data gathered with the 785-nm spectrometer. This device consisted of a multi-mode fiber laser BWTEK BRM-OEM-785 (785 nm), a Raman head BWTEK BAC100-785E and an objective lens Zeiss Epiplan 50×/0.50 infinite/0 44 28 50 M20.32 mm (focal length). The maximum output of the laser through this lens was approximately 165 mW; the laser spot diameter measured on the samples was 48 microns. The spectrometer was a BWTEK Prime T BTC661E-785CUST, covering a spectral range of 0–3000 cm^{-1}, with a resolution of 5 cm^{-1} and a CCD Hamamatsu S10141-1107S operating at −10 °C. Over 20 surface spots showing evidence of failure were analyzed to determine the chemical and orientation changes of the molecular chains and/or atomic rearrangements, in order to facilitate the understanding of the mechanisms associated with localized polymer failures caused by the adhesion of salmon muscle to the PET coating in time.

3. Results

3.1. XRD Characterization

The PET-coated ECCS multilayer composite employed in the fish processing industry for salmon canning was characterized after the application of urea solution by XRD.

The X-ray diffraction patterns showed an amorphous halo typical of polymer materials. The convex curve of the first part of the profile showed the coexistence of PET peaks due to the crystalline features of the material (Figure 2). Furthermore, it was possible to observe the well-defined peaks of the crystalline phases of the lower layers of the material: *i.e.*, tetragonal rutile TiO_2, which constitutes part of the protective coating and provides the light color to the PET polymer; iron-based oxides, being the base steel of the container; compounds based on chromium oxides that protect the steel plate from corrosion and defects occurring in the PET coating (pores and/or scratches); and urea compounds employed to detach the salmon proteins adhered to the PET coating in order to determine the defects caused on the polymer surface by their localized adhesion.

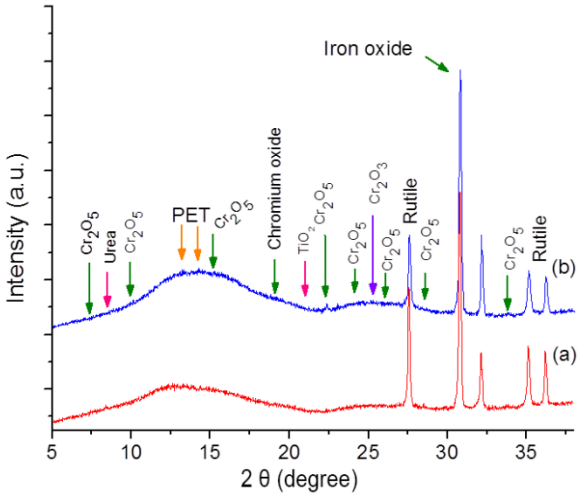
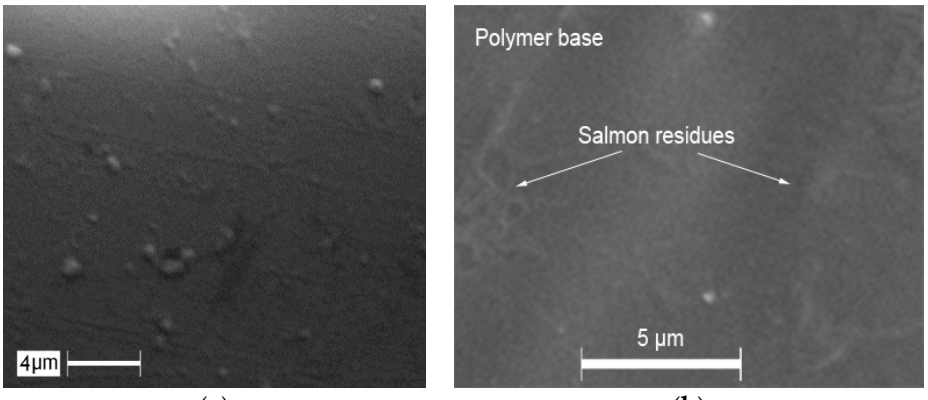


Figure 2. Diffraction pattern between 5 and 35° (2θ) of the multilayer materials that form part of the container's structure. (**a**) Spectral pattern of PET and (**b**) components of the multilayer material.

It must be noticed that from the crystalline point of view, no significant information was detected by XRD analyses with regard to the biological effects or likely alterations of the macromolecular source on the surface of the material. The evidence of chromium oxides (Cr_2O_5) not present in the original multilayer composite design (Cr^0 and Cr_2O_3) indicated that the PET polymer had detached from the underlying coating. In addition, the presence of iron oxide also confirmed the microstructural discontinuity of the thin protective chromium layers and, therefore, the detachment of the PET polymer.

3.2. Characterization of Microstructural Morphology by SEM

When analyzing these localized zones by SEM, which exhibited discoloration on the protective polymer resulting from the adhesion of salmon muscle portions (Figure 1), we could notice a clear surface quality contrast between these areas and those not affected by the adhesion. Figures 3 and 4 show such contrasting surface zones on the PET coating.



(**a**) (**b**)

Figure 3. (**a**) The PET surface is homogeneous and free from defects, showing no adhesion of salmon muscle; (**b**) PET surface showing remnants of salmon muscle and displaying a heterogeneous morphology.

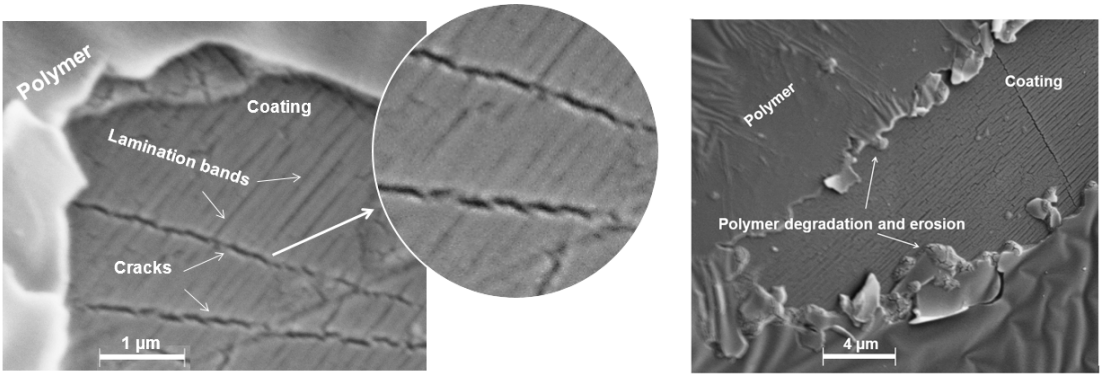


Figure 4. PET surface exhibiting persistent adherence of salmon muscle in food cans stored for 12 months; damage morphology of the different layers in the food can.

The PET surface without evidence of adhesion showed a homogeneous surface indicative of the continuing protective barrier that preserves food in time and prevents interactions with the multilayers, which otherwise when damaged may lead to degradation of the material. The PET-coated ECCS plate is biaxially oriented as a result of the manufacturing processes, a feature that is associated with good abrasion and degradation resistance against the canned food products.

When denaturing proteins with urea solution, localized residues remain strongly attached to the PET surface through binding chemical forces. It has been suggested that the carbonyl group in the ester bond of the PET coating is engaged to form hydrogen links with the amino group of the protein, which would explain the adhesion of salmon to the food container.

Upon removal of the salmon muscle from the polymer coating (Figure 4), we could observe a damaged surface morphology expressed as longitudinal microcracking, which traversed across the lamination direction of the steel. This implies deterioration of the chromium layers exposing the base steel of the container due to degradation of the PET polymer.

Figure 4 depicts polymer vestiges and salmon muscle residues or denatured proteins adhered to the steel surface with partial damage of the chromium multilayers, thereby exposing the steel to eventual physicochemical actions of the canned food.

Hence, there is localized degradation of the PET polymer and loss of the chromium layers underneath the adhered salmon muscle with a concomitant loss of functionality of the multilayer composite.

The polymer degradation and disruption of the bonds between the chromium layers and PET polymer produced by the salmon muscle components and evidenced in Figure 4 may possibly have translated into the passage of homopolymers to the food due to the breaking up of the chemical link between the carbonyl group of the benzene ring and the Cr^{2+} of the metallic coating with loss of adhesion between the polymer and the chromium deposit, producing a damage phenomenon very similar to the effect of NaCl on the ECCS-PET composite [17].

All of these factors are controlled with adequate heat treatments to preserve food, as well as appropriate storage temperatures. In this study, food cans were sterilized at 60 °C for 60 min as a standard procedure and stored at room temperature before opening. Therefore, most likely the surface was damaged as a result of the natural effect of the small muscle portions adhered to the coating, which degraded the surface in time and turned it into another color. These changes were only encountered on the polymer surface and did affect the organoleptic properties of salmon. These surface failures may consequently facilitate the electrolytic activity between the food and the metal substrates, generating physicochemical processes of corrosion due to the loss of the polymer's protective capacity [11]. On the other hand, its localized degradation deteriorates the functional integrity of the PET polymer required for optimal recycling and to reduce the impact of wastes requiring disposal.

3.3. Confocal Raman and Micro-Raman Imaging Spectroscopic Characterization

The confocal Raman microscopy analyses of the surface images from the damaged samples (Figure 5) show the area of muscle adhesion and a detail of the phase changes or compounds encountered. The surface color changes are evident and representative of the PET polymer (green), the zone of adhesion (blue) and the salmon residues (red). The image also shows dark lines (upper right side) associated with microcracking on the polymer surface.

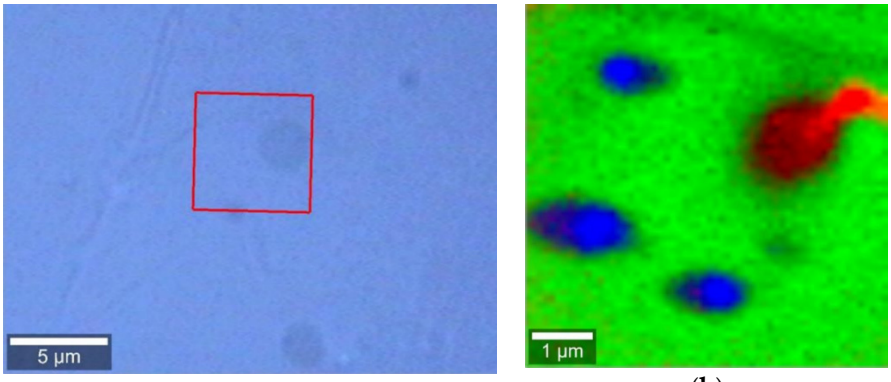


Figure 5. (**a**) The red box denotes an area of PET surface defect by salmon muscle adhesion. This section has been magnified in (**b**); (**b**) Raman image with phase changes in the area of adhesion.

Figure 6 illustrates the spectra of the colored areas in green, red and blue with surface changes from Figure 5. In all of these spectra, it is possible to see the typical rutile and PET peaks (400 and 600 cm^{-1}). Nevertheless, some differences can be noticed in some spectral regions. The red spot shows low molecular order (noticeable at the 2900–3200 cm^{-1} regions) and features of the adhered salmon.

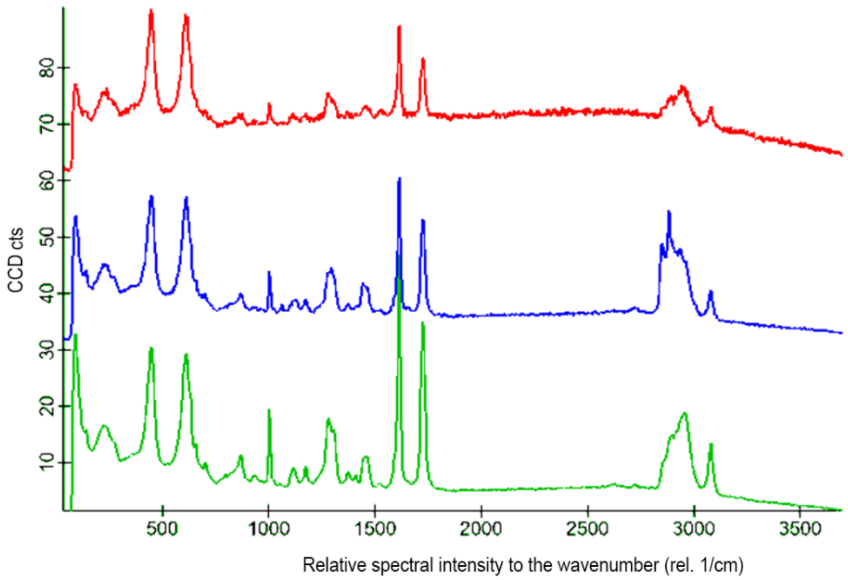


Figure 6. Average spectra corresponding to the colored areas in the sample with failure caused by persistent salmon muscle adhesion.

The blue spectrum is from an area of the PET polymer in marked contrast with the original coating as denoted by the image; whereas the red spectrum shows small changes in the bands with respect to the original PET coating. The most outstanding feature of these results was the presence of urea in

almost all of the samples, with the characteristic band ν(CN) at 1003 cm^{-1} and a variable intensity and the deformation bands δ(NH) at 1595 cm^{-1} and 2900 cm^{-1} evidencing the presence of proteins and peptides from the salmon muscle [18,19].

A second deep scan analysis was performed to determine changes in the linear phases and under the protective polymer surface, which implied no cutting or modification of the samples (Figure 7).

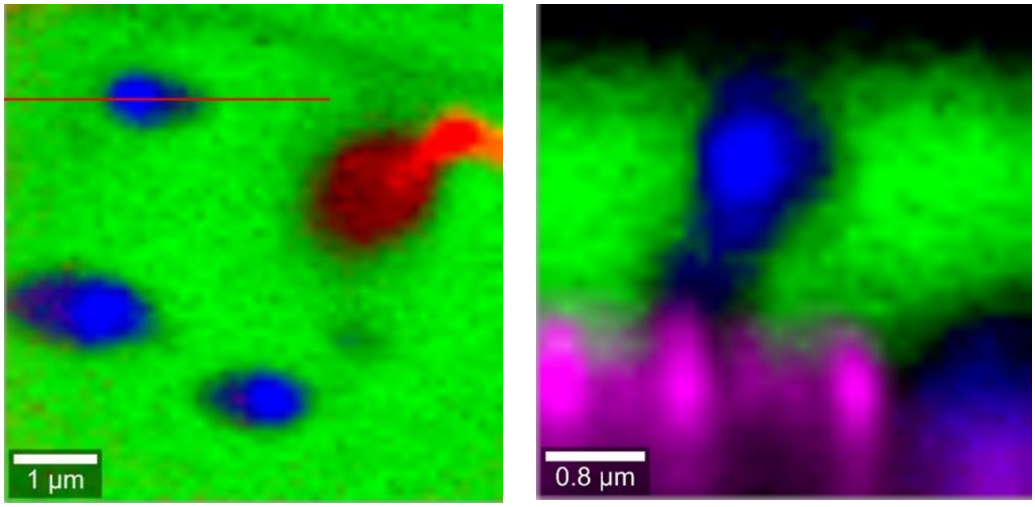


Figure 7. (**a**) Raman image in the *X*–*Y* direction; (**b**) analysis of red line zone depicted in (a) showing the position of the Raman image in depth in the *X*–*Z* direction.

Figure 7 shows the phase changes already determined, but deeper into the coating, it is possible to visualize a blue area of salmon adhesion. The effect of this adhesion can be noticed beneath the surface, producing microstructural changes that compromise part of the polymer thickness. The other colored areas under the PET (green) are associated with microconstituents of the polymer near the polymer-metal interface of the can.

Figure 8 represents the spectra of the Raman *X*–*Z* images from Figure 7, characterizing the different phases observed and especially the area of adhesion that generates a change of functionality given the microstructural alterations in the polymer coating.

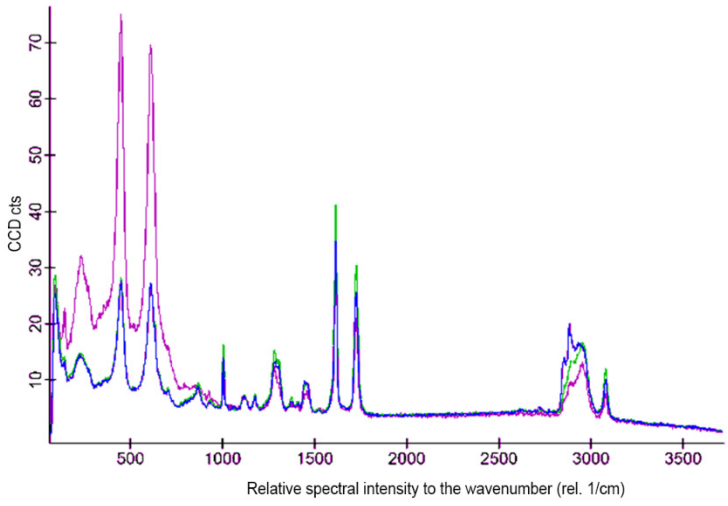


Figure 8. Average spectra corresponding to colored areas in *X*–*Z* from Figure 7.

These spectra show also the typical structure of the coating and interface with the metal (rutile and PET). The areas of adhesion show a low polymeric order (caused by degradation) as manifested by changes in the width and intensity of peaks and the bands that can be attributed to salmon residues. The band at 144 cm^{-1} attributed to anatase is noticeable, the polymorph of rutile, which was not expected to be present in the coating, and therefore, it can be considered as an impurity.

The presence of PET was predominant in such spectra; however, small amounts of elongated rutile particles were detected as indicated by the spectral peaks (Figure 7b). PET alterations in the areas of adhesion were confirmed in the same bands indicated in Figure 6, varying in intensity from the surface to deeper zones of the area analyzed in the degraded samples, which initially manifested as color changes resulting from the adhesion of muscle to the container wall.

Raman spectroscopy analyses were performed to validate the results concerning degradation and localized failures of the protective coating. In that sense, Figure 9 shows the spectra measured in areas of Sample 1 degraded by the adhered salmon muscle (red) and corresponding to points exhibiting surface color changes from white to yellow, as seen in Figure 1; it also shows the low-frequency spectral plots, those bands showing the greatest spectral differences in Sample 2 (green) and treated with urea solution.

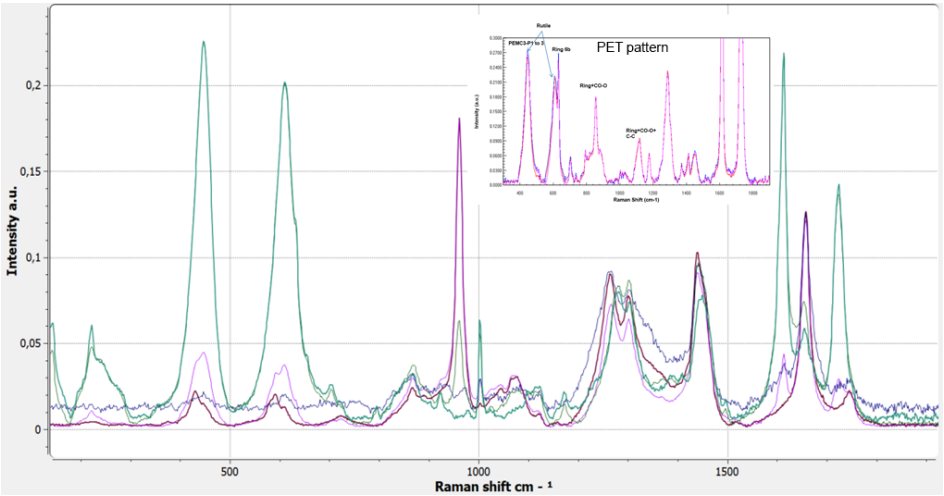


Figure 9. Raman spectra from Samples 1 (**red**) and 2 (**green**) corresponding to surface spots showing color changes after salmon adhesion.

We must notice the appearance of new bands related to the yellow spots in Figure 1 and with the spectra observed in Sample 2; these bands are mainly those seen at 960 cm^{-1}, 1260 cm^{-1}, 1300 cm^{-1}, 1440 cm^{-1} and 1657 cm^{-1}. These resonance waves are not attributed to vibration modes in the PET coating or to the rutile load that gives the white color to the polymer. A set of spectral measurements performed on different salmon samples identified that these bands are mostly the product of salmon residues adhered and interacting with the polymer coating, ultimately affecting its crystallinity [20].

4. Discussion

The localized PET polymer degradation characterized by SEM and caused by the salmon muscle adhesion in time shows evidence of physicochemical interactions occurring in the system. As a result of the above, the chromium layers are exposed and partially degraded, especially in the direction of the steel laminate, altering the composite's performance, since the multilayers cease to play their protective role. Regarding the chromium layers, specifically in those areas exhibiting damage, they do not perform their passive function of protecting the base steel, which may in turn lead to corrosion processes.

The cause of this degradation originated in the organic material or biopolymer, which is mainly composed of proteins and lipids [19]. Lipid oxidation processes occur as a series of reactions in the

free-radical chains and lead to complex chemical changes that negatively affect the quality of food [20], such as the accumulation of lactic acid from postmortem glycolysis and decreased pH [21].

Other studies [22,23] have found that 1% lactic acid on chromium-passivated tin plates and protected by organic compounds can be attacked by corrosion currents due to the presence of pores and interfacial defects that allow degradation and loss of functionality at pH 2–3. The postmortem salmon produces lactic acid and may be one of the sources of organic acid that may act on the container-food system.

The application of hydrophobic products, such as organosilane precursors employed in other applications, may be an option to neutralize and minimize the effect of the adhesion characterized in this work [24].

Thus, our future studies should be focused on determining the concentrations of lactic acid in canned salmon in time and on measuring the effects on the ECCS-PET under controlled potentiostatic conditions. This will allow elucidating the timing of physicochemical interactions for the localized salmon adhesion to the polymer surface of the can wall and the effects on the properties of the multilayer composite.

On the other hand, the spectroscopy analyses showed a correlation with the SEM observations regarding the presence of not only surface changes, but damage to the layers involving microstructural and functional changes of the multilayers, either by atomic rearrangements or phase changes.

The spectroscopy results showed clear differences between the spectra acquired from samples treated with urea solution and those from the control Sample 1 exhibiting commonly-occurring natural adhesion. Some other bands of urea appear as a shoulder or small contributions to the functional groups of PET. It is interesting to note that the main vibrational bands of the PET coating remained practically unaltered under this urea solution treatment employed to denature and detach the salmon muscle.

It is particularly important to emphasize that the spectra of Samples 1 and 2, taken from areas with hardly any PET degradation, are different from those of areas showing evidence of damage.

However, the spectral region 2700–3000 cm^{-1} (Figure 8), corresponding to ν(C–H) vibrations, presents important differences in intensity.

Concerning Figures 6, 8 and 9 the vibrational spectroscopy analyses show differences in the band at 1200 cm^{-1}; corresponding to changes in polymer crystallinity, atomic rearrangements and stretching of chains mainly observable in the bands at 960 cm^{-1} and 1300 cm^{-1}, as well as adhesion of proteins and peptides to the protective polymer coating in the range of 2900–3200 cm^{-1}.

Detailed information on the origin and processing practices of salmon muscle for canning and on proteomic studies of these samples will allow us to identify the compounds formed by the denaturation of the proteins adhered and thermally affected by the sterilization process during canning.

5. Conclusions

The multilayer metal-polymer composites are designed for potential performance in packaging applications; however, concerning canned salmon, such a performance may vary from the expected behavior given the food-container interactions. The components determined by XRD have different specific functions that must remain intact to preserve the canned food in time.

The surface polymer failures in areas of salmon adhesion in cans were evaluated after 12 months of storage at room temperature. After the removal of proteins by urea solution, it was evident that some areas were degraded, as indicated by the surface color changes on the PET coating. The effect in time translates as a phase change by the presence of residues, proteins and peptides from the salmon muscle that impregnate the polymer surface and below as determined by Raman imaging.

The SEM characterization of such adhesion zones indicated a change in morphology from homogeneous and continuous to a microcracked surface, degrading the PET coating and favoring the physicochemical activity between the stored product and the metal substrate; this, especially because the damaged chromium ceases to perform cathodically and exposes small areas of steel, limiting therefore the useful life of the container. The use of urea solution in the area of failures did not affect

for the most part the microstructural properties of the PET coating, either as an increase in crystallinity or amorphism.

It was the activity of the salmon muscle that produced the degradation of the polymer through mechanisms based mainly on the biochemical and chemical components of the muscle, such as peptide oxidation, changes in pH by the lactic acid production of the postmortem salmon and eventual contaminants present during the canning process.

The vibrational spectroscopy analyses of the adhesion zones made evident the microstructural instabilities of the PET coating, with the loss of surface integrity expressed as small changes in crystallinity, which is associated with changes in its inherent properties, such as decreased abrasion resistance and corrosion resistance against aggressive canned food products. The presence of failures make it necessary to recommend the strengthening of the PET surface by increasing its hydrophobic properties through the incorporation of organosilanes, among other compounds, to prevent the adhesion of salmon to the container walls.

The surface failures and consequent degradation of the coating by the adhesion of food products to the PET polymer limit the life cycle and reprocessing of these materials into new applications to reduce the environmental impact due to the loss of functionality of these multilayer composites.

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Author Contributions: Ernesto Zumelzu is the principal investigator and director of the project; María José Wehrhahn conducted the experiments on adhesion studies; Fernando Rull was in charge of the vibrational spectroscopy characterization; Héctor Pesenti performed the X-ray diffraction characterizations; Aurelio Sanz-Arranz provided the technical support for the spectroscopy analyses of samples; and Ricardo Ugarte characterized the degradation of the composite's layers.

Conflicts of Interest: The authors declare no conflict of interest.

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