

## Research Article

# Evaluation of NaCl Effect on Vibration-Delaminated Metal-Polymer Composites by Improved Micro-Raman Methodology

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Polyethylene terephthalate (PET) is a polymer coating that protects the electrolytic chromium coated steel (ECCS) against aggressive electrolytes like NaCl. It is widely accepted by manufacturers that NaCl has no effect on the PET coating, which is inert. However, we showed that there are some effects at the structural level, caused by vibrations, and facilitated by defects on the layers. The vibrations occurring during the transportation of food containers produce delaminations at given points of the metal-polymer interface, known as antinodes, which in turn may produce PET degradation affecting food quality. The former can be determined by electrochemical measurements, and the changes in composition or structural order can be characterized by Raman. The present work applied this latter technique in experimental samples of PET-coated ECCS sheets by performing perpendicular and parallel analyses to the surface, and determined that it constitutes a new potential methodology to determine the behavior of the composite under the above conditions. The results demonstrated that the delamination areas on the PET facilitated polymer degradation by the electrolyte. Moreover, the Raman characterization evidenced the presence of multilayers and crystalline orderings, which limited its functionality as a protective coating.

## 1. Introduction

The adhesion in PET-coated ECCS plates is mainly explained by its structural constituents. It is well known that the chromium deposit on the ECCS plate consists of  $\text{Cr}^0$  and  $\text{Cr}^0 + \text{Cr}^{n+}$  ( $n = 2, 3$ ). Polyethylene terephthalate is manufactured by the polycondensation reaction of ethylene glycol and dimethyl terephthalate. To achieve the metal-polymer bonding, the chromium uses the oxygen of the PET to form links similar to those of the oxide with which good adhesion of the polymer to the ECCS plate can be achieved. In the chromium-benzene ring chemical bonding, there are four chromium electrons ( $\text{Cr}^{2+}$ ), that is, two electrons from each oxygen atom in both carbonyls. The benzene ring of the PET contributes up to six electrons in pairs according to the structure of the delocalized orbitals of benzene. As the oxygen molecules come closer, the  $\text{Cr}^{2+}$  acts like an acid

and the benzene ring and oxygen atoms like a base, and the electrons exchange gives rise to covalent bonds. This explains the strong adherence between the PET coating and the chromium deposit on the ECCS plate [1].

The delamination of polymer protective coatings on metals, under humid environments, is associated to a complex number of physicochemical phenomena [2–4]. One of the widely accepted mechanisms is that the reaction forces involve the formation of electrochemical microcells with different anodic and cathodic zones which lead to detachment. These can cause metallic corrosion products at the metal-polymer interface level, which due to volume changes exert surface pressures facilitating delamination. We found that the electrolyte acetic-acetate produced degradation of the PET coating, inducing chemical and structural changes [5]. When studying the mechanical effects on the metal-polymer composite during drawing and mechanical compression

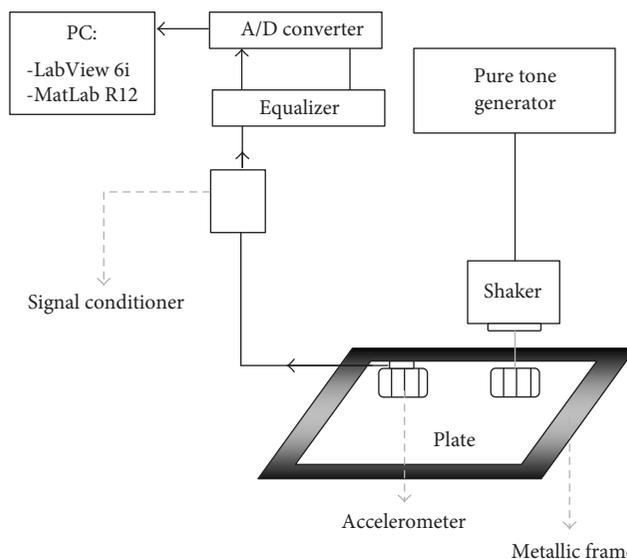


FIGURE 1: Experimental mounting of sample for vibration analyses.

loads, the PET experienced structural changes with loss of crystallinity and molecular rearrangements [6].

On the other hand, we have studied the effect of NaCl on PET-coated ECCS sheets, and the present research has detected small variations in the polymer structure by Raman techniques, even though several authors have stated that PET remains unaltered when in saline solutions [7–9].

In this study, we hypothesized that the interaction of a saline solution with delaminated areas, attributable to the displacement of the PET coating at the interface level or of areas in contact with the metal (antinode zones produced by mechanical vibrations), may induce changes in the chemical ordering of the PET layer. Hence, the main objective was to characterize and evaluate the changes produced by the NaCl solution through micro-Raman techniques, analyze the spectral changes in the directions of the coating at  $X$ - $Y$ - $Z$ , determine the occurrence of delamination facilitating composite degradation by the electrolyte used, and recommend actions to prevent this type of failures in PET-coated ECCS food cans in order to prolong their service life and thus reduce the negative impact on food quality. PET films are often coated with layers of other polymers to optimize performance in various applications, such as promoting the adhesion of lacquer and metals. Micro-Raman techniques can also evaluate these layers. The ideal performance implies preserving the food properties during canning processes [10].

## 2. Materials and Methods

The manufacturing of PET-coated ECCS samples requires the protection of steel by a polymer coating, which is applied by bathing the steel in PET under time- and temperature-controlled conditions, and the employment of thermal treatments to obtain high performance canning materials. The chemical composition (%wt) of steel was 0.074% C, 0.260% Mn, 0.021% P, 0.016% S, 0.032% Al, 45 ppm N, and Fe (remaining percentage).

PET-coated ECCS samples with point delaminations, that is, displacements of the PET polymer coating from the surface in contact with the steel, called antinode points, and produced by mechanical vibration tests, were selected and characterized [11, 12]. A schematic design to produce vibrations can be observed in Figure 1.

To this end, an electrochemical experiment employing 3.5% sodium chloride w/v was performed, allowing the system to stabilize for two hours (evolution of the open circuit potential). Later, an anodic overpotential of 60 mV, with respect to the potential measured in the open circuit, was applied. For this purpose, a silver/silver chloride (Ag/AgCl) electrode, and a platinum auxiliary electrode at 20°C for thirty minutes was employed, resulting in the current versus time plot,  $I(t)$ , whose integration provided the electric charge transferred during the oxidation of the metal surface. Subsequently, the system was tested, and the spontaneous evolution of the potential difference developed between the working electrode and the reference electrode was recorded over time. Potential versus time plots,  $E(t)$ , within 2 hours of the experiment, were produced. This experiment is of interest only to evaluate possible changes or diffusion in the multilayers of the protective PET polymer. The occurrence of metal-polymer delamination points was proved by magnetic induction and ultrasound techniques using a K. Deutsch device, L 2041 CTM, ISO 2178, for nonmagnetic coatings on steel.

Scanning electron microscopy (SEM) observations were employed to identify the areas of greatest physicochemical interaction. Later, nonattacked control samples and NaCl-attacked samples were analyzed by micro-Raman to characterize the behavior of PET as a protective coating of steel. This study was performed by means of a Raman instrument consisting of a spectrometer (Kaiser Holospec f/1.8i, spectrum range 100–3800  $\text{cm}^{-1}$ , and a spectral resolution of 4  $\text{cm}^{-1}$ ); a CCD detection system (Andor DV420A-OE-130); an illumination source consisting of a helium-neon

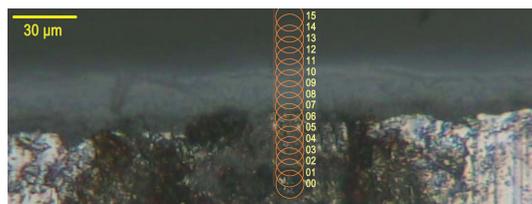


FIGURE 2: Positions of points for micro-Raman analyses perpendicular to the surface of sample.

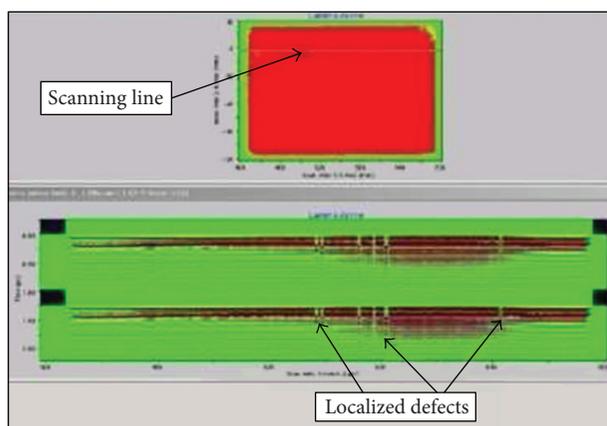
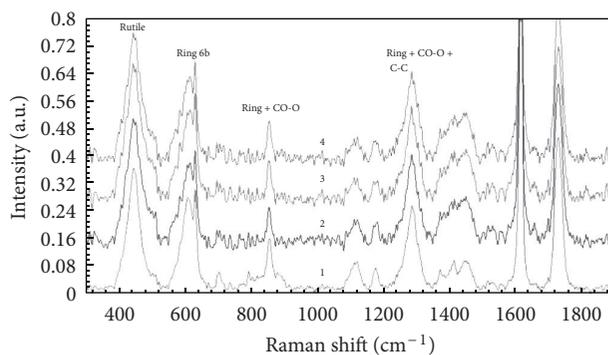


FIGURE 3: Linear scanning of metal-polymer composite showing delamination points at the interface.

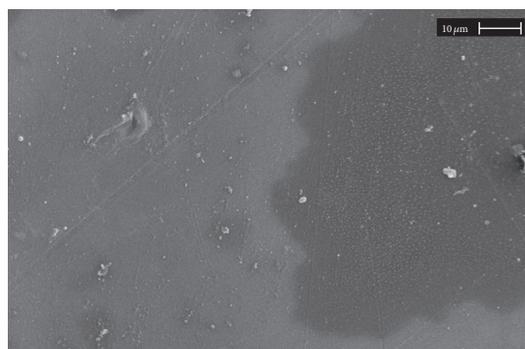
(He-Ne) laser at 632.8 nm (Melles-Griot 0.5-lhp-151); a Nikon Eclipse E600 1000x microscope supplied with a JVC TK-C1381EG telecamera. This Raman instrument was coupled by optical fiber to a microscope to analyze the samples at a microscale up to several microns. The samples were examined by making the laser beam strike perpendicular and parallel to the surface. In the perpendicular case (Figure 2), the laser struck at  $90^\circ$  on the PET coating; and in the parallel analysis, the sample was placed on its edge on the specimen holder of the microscope to determine the PET cross-sectional spectrum profile. In the second procedure, cross sections of the samples were microanalyzed parallel to the coating by Raman obtaining spectra every  $5 \mu\text{m}$  at different points starting from the PET surface until reaching the ECCS interface. The diameter of the laser spot was 10 microns approximately. At the polymer-metal interface, spectra were obtained by focusing the laser spot on the polymer.

### 3. Results and Discussion

Figure 3 shows the presence of delamination defects caused by the vibration tests, favoring the physicochemical interactions with NaCl at the metal-polymer interface. Since this work employed samples with vibration-induced delamination defects or antinodes [13], it is important to mention that such delaminations were the result of fractures and deformations of the  $\text{Cr}_2\text{O}_3$  layer at localized points, breaking up the PET-polymer/chromium-layer chemical bonds. The above is



(a)



(b)

FIGURE 4: Spectra perpendicular to the PET with macromode analyses of the samples using an FT-Raman instrument.

corroborated by SEM images, where the activity of the electrolyte was more intense in the darker areas, corresponding to polymer detachment zones. This occurred because of the lower degree of deformation of the chromium layer when compared with the PET coating, and the nonhomogeneous nature of its surface [12]. This implies that the acid-base bonds interacting between the layers are affected by the above-mentioned conditions with regard to the remaining chromium interface and ester groups. Thus, it is of interest to elucidate the structural composition of the polymer coating, and how the delaminated areas perform when attacked by the NaCl solution.

The micro-Raman analyses of the control samples, not attacked by the saline solution, showed no degradation products, which was supported by the constant spectra from the polymer coating. The spectrum analyses detected the presence of rutile as a constituent of the protective polymer, in the form of pigments, whose function is to provide the light color to the PET polymer.

However, analyses perpendicular to the PET coating (Figure 4) determined the presence of spectra showing small differences between degraded points and points without noticeable degradation in the samples attacked by the solution.

These differences were associated to the area of vibration, mainly the triplet at 1373, 1409, and  $1447 \text{ cm}^{-1}$  at points of

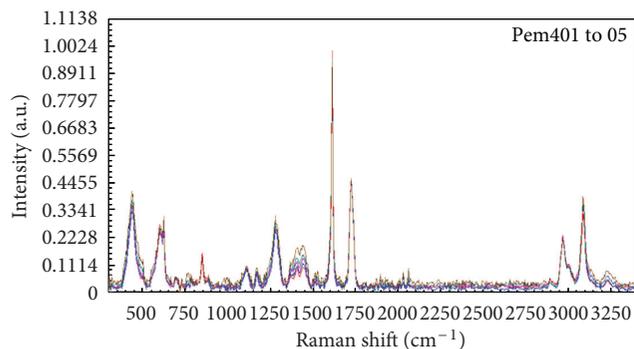
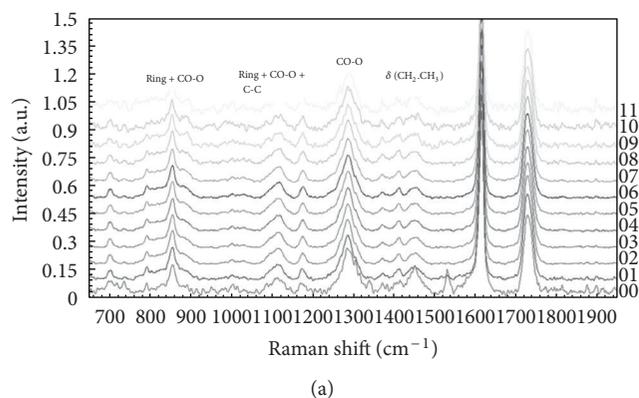
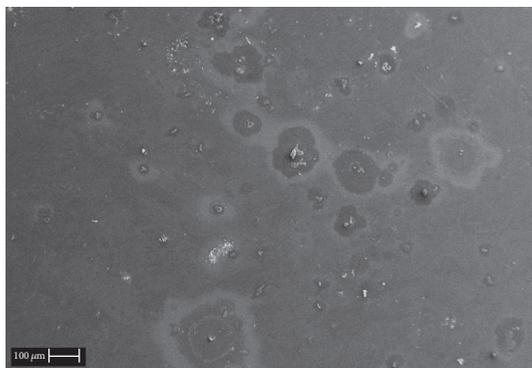


FIGURE 5: Spectra in region  $1300\text{--}1500\text{ cm}^{-1}$ , sample with antinodes.



(a)



(b)

FIGURE 6: Spectra parallel to the PET with micro-Raman analyses of cross-sections every  $5\text{ }\mu\text{m}$  from the PET surface to the ECCS interface.

CH2 and CH3 deformation. Spectrum 1 corresponds to the area without degradation (Figure 4). The bands were generally better defined than in the points without degradation. When comparing the spectrum 1 with the spectra 2 to 4, the effect of the solution on the attack points can be clearly seen. A deeper analysis of spectra in the bands  $1300\text{--}1500\text{ cm}^{-1}$  showed small differences in the deformation regions CH2 and CH3 (Figure 5).

The area with antinodes (dark) indicating delamination was exposed by the action of the saline electrolyte as seen in Figure 4 (sample M1), and Figure 6 (sample M2).

Figure 6 shows the detection of small changes in the regions  $1300\text{--}1500\text{ cm}^{-1}$  and  $800\text{--}900\text{ cm}^{-1}$ . A transition in the evolution of bands  $1100\text{--}1150\text{ cm}^{-1}$  associated with C-C and ring vibrations (ring coupled with CO-O) near the surface is also evident.

This evolution indicates that the crystallinity of the material decreases exactly when the PET coating is reached. Deformation vibrations CH3 and CH2 in the region  $1400\text{--}1500\text{ cm}^{-1}$  are also consistent with this interpretation. The changes or alterations detected by Raman occurred repeatedly in various samples, providing a higher degree of certainty of the results obtained. It must be considered that the perpendicular and parallel analyses started from the PET surface in contact with the metallic layer until the ECCS interface involving a thickness up to 5 microns. The surface spectra are lighter, and the alterations detected cannot be associated to signal-to-noise ratios in the spectroscopy analyses. The Raman analyses also evidenced the existence of polymer multilayers that help in the metal-polymer adhesion and provide protection to the steel. Thus, important changes were detected at the transition level between the base metal and the first layer of the coating, as shown in Figure 7.

These changes were caused by the inclusion of a polymeric compound between the PET coating layer and the steel plate. The presence of bands at  $1530\text{ cm}^{-1}$  (the most intense) and  $710\text{ cm}^{-1}$ , and an overlapping in region  $1600\text{ cm}^{-1}$ , was observed. These bands were consistent with the presence of a “nitrile” compound, which makes the material be multilayered and contributes to the chemical adherence of the PET to the metal layer at the interface level. Spectral variations were also observed in the CH vibration zones ( $2960$  and  $3081\text{ cm}^{-1}$ ), near the contact of the PET with the metal, and were consistent with those observed at low frequencies.

Finally, given the characterization evidence, the delamination damage detected, and the electrolyte attack observed, it is important to consider how to minimize or eliminate the occurrence of detachment between layers caused by the vibrations and leading to the presence of antinodes that induce structural modifications in the viscoelastic layer covering the surface of the steel plates. In this regard, it is required to ensure continuous and thicker chromium and chromium oxide layers to strengthen the bonds with the ester groups of the PET coating, as well as to achieve steel surfaces with a controlled roughness during manufacturing either through polishing and/or chemical baths, all of which are matters for future actions in this line of research.

#### 4. Conclusions

The performance of composite coatings employed in food containers was investigated using a novel technique consisting of vibrations to induce delaminations of the layers, electrochemical measurements, and perpendicular and

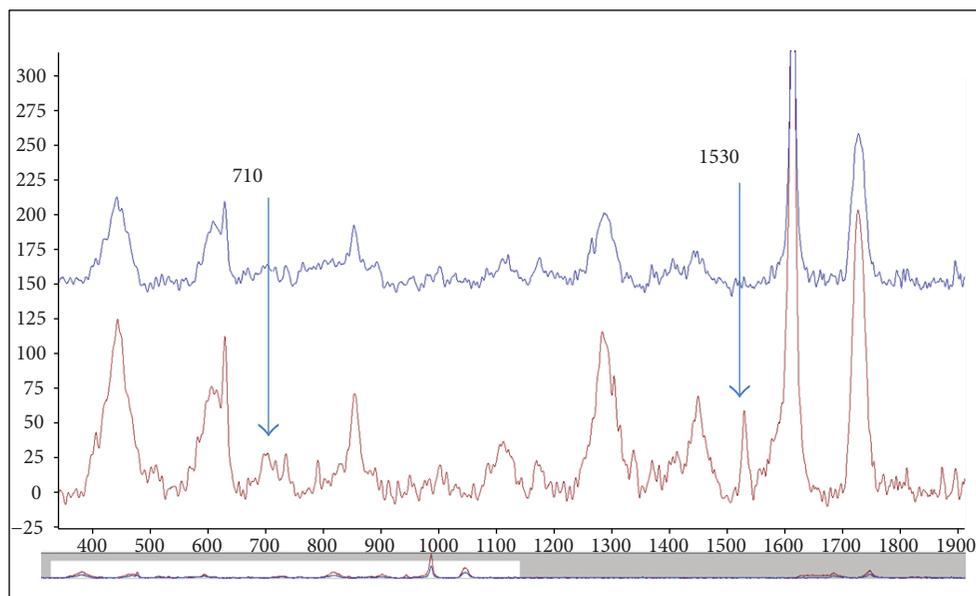


FIGURE 7: Micro-Raman analysis parallel to the PET surface indicating the presence of another compound of type “nitrile.”

parallel analyses to the surface of the coating, and the results permitted the following conclusions.

- (1) The PET-coated ECCS samples exposed to a sodium chloride aqueous solution showed only small differences in the polymer coating between the degraded and nondegraded points. The spectral differences detected by micro-Raman affected mainly the vibrations, such as  $\text{CH}_2$  deformations, and  $\text{CO-O}$  and  $\text{C-C}$  chains.
- (2) The combination of both the perpendicular and parallel observations of the PET coating played a key role in the analyses. After examination by making the laser beam strike parallel to the surface to determine the spectrum profile, depending on the distance from the metal to the surface, the presence of another compound at the PET-metal interface was noticed. This compound was of type nitrile and contributed to the adhesion of the PET to the base metal.
- (3) The protective capacity of the PET polymer will depend on the  $\text{Cr}$  (0) and  $\text{Cr}_2\text{O}_3$  layers continuity; thus, their homogeneity will favor stronger acid-base bonds and will minimize delamination resulting from vibration effects. The adequate control of these bonds will prevent adverse effects on the PET coating resulting from the physicochemical interactions with the  $\text{NaCl}$  solution at the interface level, and consequently prevent an adverse impact on food quality.

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