Characterization of metallic materials used in food packaging

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Abstract. The work represents a comparative study of three types of metallic food packaging used in Romanian food industry. In this paper, three food packaging made of low-alloy steel were analyzed. To characterize their properties, spectrometric analyzes were performed to determine the chemical composition, microhardness analyzes, optical microscopy and Fourier Transform Infrared Spectroscopy. The investigations on the three samples were achieved through X-ray Fluorescence Spectrometry (XRF) analysis performed with a Spectro XEPOS analyzer, optical microscopy analyzes performed on a Reichert UnivAR optical microscope, and microhardness tests by the Vickers method using the CV - 400 DTS tester / 2 (CV Instruments) and Fourier Transform Infrared Spectroscopy (FTIR) with JASCO 6200 analyzer, equipped with Golden Gate type attenuated total reflection (ATR) device. Following the investigations, the presence of epoxyphenolic resin was confirmed in the case of the first two samples and a layer of polyester in the case of sample three. Finally, conclusions are presented about the qualities of the selected packaging and their properties to keep safe the packaged products for a period of several months to several years.

1. Introduction
Packaging technologies, packaging materials and packaging have dynamically evolved in the past decades, thus ensuring that packaging has a complex functional and expressive role.

The selection of the material for the packaging and the packaging method implies a deep knowledge of them and the processes that take place in the preserved products, during the storage period [3].

They may undergo various chemical reactions with substances from the package, or may be impregnated with various toxic or odors substances.

The properties to be considered, related to food distribution, are many and may include gas or water vapor permeability, mechanical properties, sealing capacity, thermoforming properties, (resistance to water, grease, acid, UV radiation, light, etc.), machinability (on the packaging line), transparency, anti-condensation capacity, printing capacity (printability), availability and of course cost.

Conventional food packaging materials currently used vary between metals, paper, glass, and plastics [4]. Metal packaging is made from steel or aluminum. Steel is used in the production of containers for packaging a wide range of products, such as food, paints, etc [7]. Aluminum packaging is used to make containers for food and beverages, foils and laminates.

Metallic and alloys packaging is mainly used in the food industry in the packaging of canned meat, fish, fruits and vegetables, alcoholic and non-alcoholic beverages. Consumer opinion is less favorable to metals because they can influence the taste of packaged products.
The metallic packaging is made from tinplate [1], aluminum and combined materials (plastics, cardboard and metal). Recently, the weight of aluminum packaging and aluminum alloys has increased due to the advantages that these materials offer [5][6].

The following type of packaging is made from metallic materials: metal boxes, aluminum cans, metal drums and barrels, aerosol (spray) type packaging, deformable tubes. Metal boxes are used in the food industry for food packaging and preservation. The packaging system, the material used and the type of packaging must ensure the stability of the food, prevent the transfer of toxic substances from the packaging material or during the packaging process to the food, avoid exchange of moisture with the environment, impurity with unwanted substances in the environment, contamination with microorganisms and favoring photochemical reactions or caused by microbiological contamination.

The advantage of metal boxes is rigidity, avoiding thus the risk of breakage during transport.

Smart packaging (or Intelligent packaging) has been gaining publicity lately, with an expected market of $26.7 billion by 2024 [2]. Smart packaging represents packaging systems carrying sensors that help prolong the shelf life of foods, reveal information on freshness and quality, and enhance the safety of the product and consumer.

Another technology in packaging systems is active packaging, which is the integration of additives with the packages to improve food shelf-life and quality [8].

2. Materials and methods

2.1. Materials used in the study

For the study, three types of metallic food boxes were selected from various manufacturers (figure 1), and were cut from the bottom of the boxes, with a diameter of 40 mm, which were then subjected to spectral chemical analysis, optical microscopy, microhardness analysis and Infrared Spectrometry with Fourier Transform.

![Figure 1. The three metallic food packaging samples](image)

2.2. X-ray Fluorescence Spectrometry (XRF)

The XRF Analyzer spectrometer used for the elementary analysis of the samples of interest for this research it was Spectro XEPOS type. The analysis was performed according to the requirements [15] of the SR EN ISO 17025: 2018 standards, using the TurboQuant Alloys analytical program. Method parameters: supply voltage: 120V / 230V a.c. ± 10%, 50/60 Hz, for quantitative analysis methods: Fundamental Parameters and TurboQuant, analysis in helium atmosphere, detects elements from Na to U from the periodic table, SDD - Silicon Drift Detector with cooling system, stable peak position and high detection rate (120 kcps); X-ray tube with Pd anode, maximum power of 50 W, high tube voltage 50 kV [14].
2.3. Optical microscopy
The optical investigations, made on three polished samples, were performed on a Reichert UnivaR microscope, viewing can be done in bright field (BF), dark field (DF) and in simply reflected polarized light. It was used a compact Hitachi KPF1 digital camcorder, lightweight CCD camera, color, integrated type, using the latest 2/3 inch CCD image size type, with CCIR signal type; The actual 782x582 pixel count in combination with a high-density montage. The Analysis Program is Omnimet Express, which includes a powerful database and report generator that allows you to store images and their associated data to generate a report.

2.4. Microhardness
The Vickers microhardness tests were performed using the CV - 400 DTS / 2 testers (CV Instruments), with the following characteristics: loading force 200 gf and the action time was 30 s.[13]

2.5. Fourier Transform Infrared Spectroscopy
Fourier transform infrared spectroscopy (FT-IR) was used to determine the chemical structures of some inorganic substances, which is one of the methods we can perform a qualitative and quantitative analysis of organic compounds. The analysis was performed with a JASCO 6200 analyzer, equipped with a Golden Gate type attenuated total reflection (ATR) device.

3. Results and discussions
3.1. Spectrometry results
Following the XRF analyzes (Tables 1, 2 and 3), the mass concentrations of the 4 main elements were determined. [15] Variations in Fe concentrations can be observed in the case of the three samples between 79-84%.

| Table 1. Chemical composition analysis (XRF) of sample 1 |
|---------------------------------------------------------|
| Symbol | Concentration, % | Standard deviation  |
|--------|------------------|------------------|
| Al     | 10.98            | 0.01             |
| Fe     | 84.86            | 0.05             |
| Co     | 1.960            | 0.048            |
| Sn     | 0.7817           | 0.0020           |
| C      | 0.06             | 0.0015           |
| Others | 1.3583           | -                |

| Table 2. Chemical composition analysis (XRF) of sample 2 |
|---------------------------------------------------------|
| Symbol | Concentration, % | Standard deviation  |
|--------|------------------|------------------|
| Al     | 14.11            | 0.01             |
| Fe     | 81.70            | 0.05             |
| Co     | 1.828            | 0.043            |
| Sn     | 0.8499           | 0.0020           |
| C      | 0.06             | 0.0013           |
| Others | 1.4571           | -                |
Table 3. Chemical composition analysis (XRF) of sample 3

| Symbol | Concentration, % | Standard deviation |
|--------|-----------------|--------------------|
| Al     | 17.14           | 0.02               |
| Fe     | 79.01           | 0.05               |
| Co     | 1.726           | 0.041              |
| Sn     | 1.156           | 0.003              |
| C      | 0.06            | 0.0012             |
| Others | 0.908           | -                  |

Following these determinations, the brand classification is as follows: STEEL C4D1, low carbon steel according EN 10016-3 (1994); ISO / FDIS 16120-2 (2001), with the following properties: density 7.8-7.9 g/cm³, elastic modulus 200-215 GPa, melting point 1480-1526 °C.

3.2. Optical microscopy results

Qualitative microscopy studies were performed on three cans, of different producers, but from the same type of material, respectively ferric steel covered with a protective layer. Thus, the samples taken from the three cans were cutted in cross section and they were prepared for quantitative metallographic analysis.

For the layer thickness measurements were performed eight fields with magnification of 80 x. A comparable layer thickness can be observed, at the first test the degree of non-uniformity of the layer thickness being higher (figure 2), and the lowest degree of non-uniformity at sample three (figure 4).

Following some metallographic analyzes the thickness of the upper layer was determined. Metallographic analyzes were performed using an optical microscope Reichert Univar on cross-cut samples.

Investigations on the metallographic microscope reveals that the third sample has a uniform layer deposited on the base material and the other samples show non-uniformities in the deposited layer.

Figure 2. Optical microscopy image (X80) of sample 1 a- captured; b- processed
In the three cases, even if the samples are un-attacked, the limits of polyhedral, fine and uniform grains are observed, characteristic of a cross section through a steel sheet. The confirmation that the sheet is made of steel came from the test with the magnet, which is strongly attracted by the magnet.

From the three graphs resulting from the measurements it results that sample 1 presents a more uneven layer thickness, and sample 3 the most uniform layer thickness (figure 5-7).
Figure 5. Analysis of the evolution of the layer thickness for the sample 1

Figure 6. Analysis of the evolution of the layer thickness for the sample 2

Figure 7. Analysis of the evolution of the layer thickness for the sample 3
3.3. Hardness results

After chemical analysis and characterization by optical microscopy, the samples were subjected to microhardness tests by the Vickers method, the resulting average values being shown in the figure 8. From the obtained data it is observed that the maximum value of the micro-hardness is found in sample 3, and the minimum value has sample 1.

![Figure 8. Vickers microhardness values](image)

3.4. Fourier Transform Infrared Spectroscopy results

The Fourier Transform Infrared Spectroscopy (FTIR) spectra for the investigated sample are shown in Figures 9, 10 and 11.

In the spectra recorded for sample 1 and sample 2, between 3200 and 3500 cm\(^{-1}\), a wide absorption band of the phenolic H-O bond is observed. Between 2860 and 2970 cm\(^{-1}\) it is reveals bonds due to the stretching vibrations of the C-H bonds from the methyl, methylene and methoxy groups (CH\(_3\), CH\(_2\), O-CH\(_3\)), at 1605.45 cm\(^{-1}\) and 1505.17 cm\(^{-1}\) it is reveals bonds due to the stretching vibrations of the C = C and C-H bonds from the aromatic ring, at approximately 940 cm\(^{-1}\) it is reveals bonds due to the stretching vibration of the epoxy group, at approximately 1230 and 1178 cm\(^{-1}\) it is reveals bonds due to the vibrations of the C-O bond from the vicinity of the aromatic nucleus, and between 1100 and 650 cm\(^{-1}\) bands appear due to the vibrations of deformation of the C-H bonds from the methyl, methylene and methoxy groups.
The obtained spectra on sample 3 were similar to typical FTIR spectra of polyesters, being revealed characteristic peaks at 1712 cm\(^{-1}\) (due to the asymmetric stretching vibration of C = O bond from the carbonyl group), at 1406 cm\(^{-1}\) (due to the stretching vibration of the C-C bond in the benzene
ring), at 1242 cm\(^{-1}\) (due to the bending vibration of the C = O bond in the ester group coupled with the stretching vibration of the C-C bonds from the benzene ring), at 1093 cm\(^{-1}\) (assigned to the asymmetric stretching vibration of C-O bond of esteric group), at 1015 cm\(^{-1}\) (due to the deformation vibration of the C-H bond (methine group) from the benzene ring coupled with the stretching vibration of the C-C bond from the benzene ring), at 968 cm\(^{-1}\) (assigned to the stretching vibration of C=C bond), at 721 cm\(^{-1}\) (due to the deformation vibration of the of carbonyl group C = O coupled with the stretching vibration of the C-H bond from the benzene ring).

![Figure 11. FTIR spectra for sample 3](image)

After the previous analyzes, the sample were investigated by Infrared Spectrometry with Fourier Transform showed that on the investigated samples made from metallic materials is deposited a layer of epoxyphenolic resin (sample 1 and sample 2) and a layer of polyester (sample 3).

Epoxyphenolic resins are acid-sulfur-resistant; it evenly covers the surface, dries quickly, lasts up to 200 °C and does not give the product a foreign taste or smell.

Polyesters have high tensile strength, very good chemical resistance and are stable in a wide temperature range (-60 °C ... + 220 °C). They are impermeable to liquids and have a slight impermeability to gases.

### 4. Conclusion and perspectives

Following the XRF analysis determinations, the metallic material for the food packaging was classified as STEEL C4D1, which is frequently used for the manufacture of these types of cans.

Based on the optical microscopy analysis, in sample 3 can be observed a good adhesion between the substrate and the covered area, with relatively small layer thickness values, and for samples 1 and 2 there it is found high degrees of unevenness of different layer thickness. In all three cases, even if the
samples are unattacked, we can observe polyhedral, fine and uniform grain boundary, which is characteristic of a cross section through a ferric steel sheet.

The Vickers microhardness results show that the maximum value: 189.38 is found in sample 3, and the minimum value has sample 1: 126.28.

Fourier transform infrared spectrometry analyzes showed that a layer of epoxyphenolic resin (sample 1 and sample 2) and a layer of polyester (sample 3) were deposited on the investigated samples made from metallic materials. In case of sample 3 the FTIR spectra reveals a highlighted bands characteristic for polyesters. The FTIR spectra highlighted the presence of epoxyphenolic resins, compounds that are acid-sulfur-resistant that uniformly cover the surface of cans, dries quickly, withstands up to 200 °C and do not give the product a foreign taste or smell. Also, polyester class compounds have been identified that have high tensile strength, very good chemical resistance and are stable in a wide temperature range (-60 °C ... + 220 °C). They are impermeable to liquids and have a slight impermeability to gases.

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5. References
[1] Marsh, K. & Bugusu, B. 2007 Food Packaging – Role, Materials, and Environmental Issues Institute of Food Technologists 72 Nr.3. 39-55.
[2] Schaefer, D. & Cheung, W. M. 2018 Smart Packaging: Opportunities and Challenges Procedia CIRP 72 1022-1027.
[3] Siracusa, V. & Rosa, M. D. 2018 Sustainable Packaging. In Sustainable Food Systems from Agriculture to Industry 275-307.
[4] Geueke, B. et al. 2018 Food packaging in the circular economy: Overview of chemical safety aspects for commonly used materials. Journal of Cleaner Production. 193. 491-505
[5] (n.d.). Food packaging with Aluminium foil Retrieved from: https://alfipa.com/applications/aluminum-foil-laminates-food-packaging/
[6] (n.d.). Aluminium Foil CNBM International Corporation. Retrieved from: https://www.aluminiumchina.com/\_novadocuments/427439\?v=636512583854900000
[7] (n.d.). Tinplate and Tin Free Steel JFE Steel Corporation. Retrieved from: http://202.229.24.177/en/products/sheets/catalog/b1e-006.pdf
[8] Majid, I. et al. 2016 Novel food packaging technologies: Innovations and future prospective Journal of the Saudi Society of Agricultural Sciences 17 454–462.
[9] Atudosiei Nicole, P. Ștefănescu 2003 Principii biologice aplicate in conservarea produselor alimentare Revista Calita pt. ind. alimentara 4
[10] Nastasia Belc, Mihaela Ghiduruş, Amalia Miteluţ, Mona Popa, Petru Nicoliţă, Mira Turtoi 2006 Ambalarea modernă a produselor alimentare Editura Agir
[11] Athanasie Trutia, Iulian Ioniţă, Floriana Iova, Gabriel Stânescu 2003 Spectroscopic optica, atomica si moleculara Editura Universitatii Bucuresti
[12] Sopa S. 1995 Metode de conservare a produselor alimentare – Curs pentru studenţi Editura Tipo Agronomica Cluj-Napoca
[13] Ion Ciucă, Octavian Trante- Note de curs- Încercări mecanice
[14] Pence, I. 2011 Metode si tehnici instrumentale de analiza elementala a materialelor”, capitolul 8, "Tratat de Știința și Ingineria Materialelor” Editura Agir 5 1057-1152