

Replacing tin Coatings with Chromium Oxide Nanocomposites to Improve the Inner Lining of Low Carbon Steel Food Cans

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ABSTRACT

In regions with extreme climatic fluctuations-such as Iraq, characterized by high ambient temperatures, variable humidity, and extended food storage periods-the corrosion resistance and structural integrity of metal food packaging present critical challenges. Conventional tin-coated steel cans, though widely adopted, often fail to provide adequate long-term protection against corrosion and mechanical degradation under these harsh environmental conditions. This study proposes an innovative, non-toxic chromium oxide (Cr_2O_3) nanoparticle-reinforced polymeric coating as a sustainable and effective alternative to conventional tin linings for low-carbon steel food cans. The nanocomposite was formulated by dispersing Cr_2O_3 nanoparticles (0.1-0.3 wt.%) within a food-grade polymer matrix prepared from locally available Iraqi raw materials. The coatings demonstrated enhanced adhesion strength and corrosion resistance, both of which increased proportionally with nanoparticle content. Quantitatively, coatings with 0.1, 0.2, and 0.3 % Cr_2O_3 achieved adhesion strengths of 3.3 MPa, 3.8 MPa, and 4.0 MPa, respectively, with corresponding corrosion protection efficiencies of 74, 81, and 89 %. In contrast, traditional 0.3 % Sn-coated samples showed significantly lower performance, with an adhesion strength of 2.2 MPa and corrosion resistance limited to 45 %. Post-cyclic polarization SEM analysis revealed extensive cracking in Sn-based coatings, while Cr_2O_3 nanocomposites displayed minimal micro-pitting ($<2 \mu m$) and a ~70 % reduction in crack density. Tafel extrapolation confirmed the superior stability of Cr_2O_3 coatings, sustaining performance up to 1950 mV without significant degradation. The study validates that Cr_2O_3 nanocomposites not only surpass tin coatings in mechanical robustness and corrosion inhibition but also offer an eco-friendly, scalable solution for food packaging. Leachate biocompatibility tests further affirm their suitability for food-contact applications, making them particularly suitable for use in climates similar to Iraq's. *Prog Color Colorants Coat. 19 (2026), 175-187* © Institute for Color Science and Technology.

1. Introduction

Food packaging plays a pivotal role in preserving and maintaining the safety, shelf life, and nutritional quality of canned products-particularly meat-based foods, which

are highly susceptible to microbial spoilage and chemical degradation under extreme environmental conditions. In countries like Iraq, where summer temperatures often exceed 50 °C and refrigerated storage

is frequently inaccessible, the integrity of food can linings becomes critical for public health and product viability [1]. Metal food cans, especially those made of low-carbon steel, require inner protective coatings to prevent corrosion and contamination. Tin (Sn) has traditionally served as the industry standard due to its non-toxic nature and historical acceptance in food packaging. However, electrochemical studies reveal its long-term performance limitations under aggressive environmental conditions [2] and harsh environments, such as Iraq's hot, arid climate. Recent multiple electrochemical studies [3, 4], including this study, demonstrate that tin-coated samples exhibit significant pitting, weak adhesion strength, and uniform corrosion, especially when exposed to high humidity, temperature fluctuations, and aggressive environmental conditions typical of the Iraqi climate. Scanning electron microscopy (SEM) reveals localized corrosion zones and weakened barrier protection, leading to substrate exposure. Potentiodynamic polarization measurements confirm higher corrosion current densities for tin, particularly at elevated temperatures. A nationwide survey in Iraq found that over 35 % of canned food products exhibited signs of internal rusting, discoloration, or failure of the internal lining, primarily attributed to insufficient corrosion resistance under local storage conditions [5]. In both urban and rural areas, canned goods are often stored outdoors or in non-climate-controlled facilities, leading to thermal cycling, moisture condensation, and chemical attack by acidic or salt-rich food contents. A nationwide survey by Al-Hashemi et al. [5] reported that over 35 % of canned foods in Iraqi markets exhibited internal discoloration, rusting, or lining failure, primarily due to inadequate corrosion resistance under Iraq's climate. Canned goods stored in non-climate-controlled warehouses undergo thermal cycling and moisture exposure, accelerating corrosion and coating delamination, especially in acidic or saline food contents [6]. Although tin-coated steel remains the industry standard for can linings and is favored due to its appearance, formability, and moderate corrosion resistance, recent studies highlight its poor electrochemical stability in chloride-

rich and proteinaceous environments. Tin coatings tend to initiate pitting at potentials as low as 0.3 V [6, 7]. Additionally, the potential migration of tin ions into food has raised significant health concerns, prompting stricter regulatory measures regarding heavy metal leaching from food-contact materials [8]. In response to these limitations, research has shifted toward advanced protective coatings incorporating corrosion-resistant nanomaterials. Chromium oxide (Cr_2O_3) has emerged as a promising candidate due to its excellent chemical stability, passivating ability, and confirmed non-toxicity in food-contact applications [9]. Despite these advantages, few studies have examined its use in real-world food packaging scenarios under the challenging climatic conditions of the Middle East [3, 10].

This study investigates food-grade polymer coatings reinforced with Cr_2O_3 nanoparticles (0.1-0.3 wt. %) as a tin-free alternative for inner linings of low-carbon steel food cans. The coatings are evaluated under simulated Iraqi storage conditions using electrochemical Tafel polarization, adhesion testing, and scanning electron microscopy (SEM). The results provide valuable insights into sustainable, non-toxic packaging solutions and advance scalable, environmentally responsible food packaging technologies designed for arid and high-temperature regions.

2. Experimental

2.1. Food packaging consists of two main components

- 1- The base metal substrate
- 2- The protective coating layer

This work was based on locally manufactured metal grape leaf cans.

2.2. Chemical composition of metal cans

The chemical composition of metal grape leaf cans was analyzed at Al-Nabaa Engineering Services Co. Ltd., Baghdad, using a PMI Master Pro (S.N52Q0089) optical emission spectrometer (OES). Table 1 shows the chemical composition of the metal substrate.

Table 1: Chemical analysis of the metal grape leaf cans.

Chemical Composition	C	Fe	Cr	Al	Mn	Co	Cu	Others
Average Wt. %	0.053	99.5	0.042	0.034	0.205	0.036	0.016	0.114

2.3. Removal of the inner layer from the can surface

The inner surface of the food (Table 2) can was coated with a thin layer of food-grade polymer containing a small percentage of tin (0.3 %). To prepare the substrate, this coating was removed from the inner surface of the can. The metal can was cut into pieces of various dimensions for sample preparation. The metal samples from the can were immersed in a sodium hydroxide solution. The polymer layer was easily removed from the inner surface of the metal through treatment with a solution consisting of 50 g of sodium hydroxide (NaOH) dissolved in 500 mL of distilled water, mixed and heated on a hot plate.

2.4. Fourier Transform Infrared Spectroscopy (FTIR)

The infrared beam interacted with molecular bonds, increasing the amplitude of vibrations. Only specific frequencies of the infrared beam were absorbed because quantized vibrations occur at specific vibrational energy levels within molecules. The test was conducted at the Industrial Research and Development Center using a Japanese IRAffinity-1-SHIMADZU device, with wave numbers ranging from 4000 to 500 cm^{-1} , to analyze the molecular vibrations of the samples.

2.5. Equipment and instrumentation

The scanning electron microscope (SEM) used in this work was manufactured by Thermo Fisher Scientific, Czech Republic. The X-ray diffraction apparatus used in this work was manufactured by Angstrom Advanced, USA. The coated inner layer was analyzed using an IRAffinity-1-SHIMADZU Fourier transform infrared (FTIR) spectrometer. A JSM-IT710HR scanning electron microscope (SEM) was used to examine the surface morphology of the corroded samples. The SEM operates at voltages ranging from 3.5 to 10.0 kV with a resolution of 400 nm. This electron microscope images surfaces using high-energy electron beams. The pH of the canned meat

serum was measured as 6.46, which remained consistent across all tests. This measurement was conducted using equipment at the Baghdad Municipality/Baghdad Water Authority. Corrosion testing was performed using an MLab 200 potentiostat/galvanostat manufactured in Germany. This instrument is valuable for electrochemical research and development, quality control, fuel cell and battery testing, and corrosion research. It offers a wide measuring range of up to ± 10 V and ± 100 A with high accuracy in both potentiostatic and galvanostatic measurement modes, with the capability to measure high current densities.

2.6. Materials and suppliers

Chitosan (fungal origin): Glenthiam Life Sciences - Gu1067 (Gillingham, England), Lignin as filler ($\text{C}_{31}\text{H}_{34}\text{O}_{11}$): supplied from local markets, Carboxymethyl cellulose (CMC), acetic acid (AA), and polyvinyl alcohol (PVA): Fluka Chemicals (Switzerland), Chromium oxide (Cr_2O_3) and male gum: supplied from local markets.

2.7. Preparation of bio-coating layer

A novel coating layer was prepared consisting of a food-grade biopolymer with varying concentrations of chromium oxide nanoparticles. Different weight percentages of chromium oxide (0.1, 0.2, 0.3 %) were incorporated. The preparation process involved; (Figure 1 shows samples: (1) the metal piece before coating, and (2) bio-coating with chromium oxides cast on the glass plate).

- 1- Dissolving fungal chitosan and lignin in glycerol
- 2- Adding carboxymethyl cellulose and polyvinyl alcohol dissolved in acetic acid
- 3- Incorporating male gum and chromium oxide nanoparticles
- 4- Hot-dip application at 70°C to deposit the chromium oxide-biopolymer layer
- 5- Comparison with the baseline coating layer

The coating was cast onto a glass plate and allowed to cure for 24 hours.

Table 2: Chemical composition of the inner surface coating layer.

Component	Chitosan	Lignin	Glycerol	CMC	PVA	Cr_2O_3	AA	Male gum
Wt. %	25	20	15	5	10	5	15	5

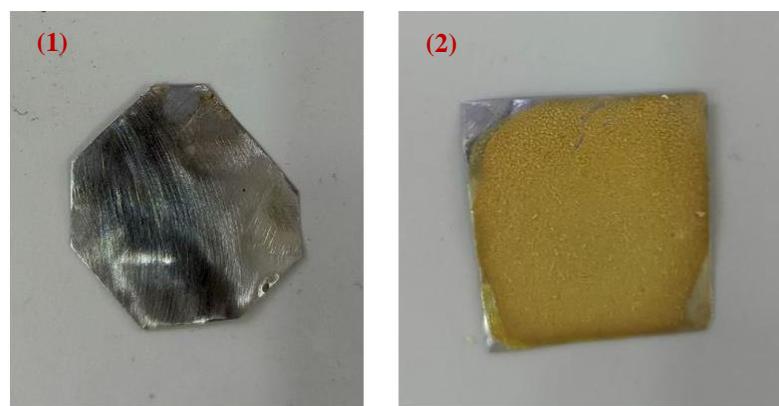


Figure 1: shows samples: (1) the metal piece before coating, and (2) bio-coating with chromium oxides cast on the glass plate.

2.8. Experiments and tests

2.8.1. Toxicity testing

Biocompatibility evaluation was conducted by administering coating samples directly to fifty mice. The animals were monitored for one month with weekly examinations. The test was performed at the Razi Center for Research and Production of Diagnostic and Medical Equipment.

2.8.2. Coating thickness measurement

The thickness of the inner coating layer was determined using an IDM 0007 device, measuring coating thickness in millimeters according to ASTM D 645 standard [10].

2.8.3. Adhesion strength measurement

The adhesion strength of the coating layer to the inner can surface was measured using an American Adhesion Tester according to ASTM International Specification D4541-09. In this test:

- Sample dimensions: 5 × 5 cm, 1 cm thick
- The sample was attached to the tester using specialized adhesive
- A vertical pulling force was applied until detachment occurred
- Adhesion strength was calculated using the equation (Eq. 1)

$$\text{Adhesion force} = \text{Applied force} / \text{Contact area} \quad (1)$$

2.8.4. Corrosion testing

Corrosion is an electrochemical reaction resulting from the interaction between a medium and metal substrate. All factors affecting both the medium and

the metal have specific impacts on corrosion behavior. Corrosion in cans is attributed to medium-related factors (moisture, salt, preservatives, etc.) and metal-related factors (coating layer properties, thickness, etc.).

The corrosive test solution was prepared by converting canned food from solid to liquid state by adding 10 g of canned food to 90 ml of distilled water, forming a simulated food solution.

The corrosion rate was measured using the Tafel extrapolation method. This method involves plotting the relationship between applied potential (mV) and logarithmic current density (A/cm²). The general equation used to determine corrosion rate based on current density in the food solution during electrochemical reactions is (Eq. 2).

$$\text{Corrosion rate (mpy)} = 0.13 \times I_{\text{corr}} \times EW/\rho \quad (2)$$

Where: I_{corr} : Corrosion current density ($\mu\text{A}/\text{cm}^2$), EW: Equivalent weight (g/equiv), ρ : Density (g/cm^3)

The electrochemical behavior and corrosion resistance were investigated using a three-electrode electrochemical cell with a volume of 250 mL containing:

1. Working electrode (test sample)
2. Reference electrode (saturated calomel electrode, SCE)
3. Counter electrode (platinum)

Electrochemical studies were conducted using a CS 310 Corr electrochemical analyzer at the Industrial Research and Development Center, Corrosion Laboratory, Ministry of Industry and Minerals, Iraq - Baghdad.

3. Results and Discussion

3.1. Toxicity and adhesion tests

The biocompatibility of the inner coating was assessed through in vivo toxicity studies using fifty mice. Throughout the one-month observation period, no mortality, abnormal symptoms, or disease manifestations were recorded, indicating that the coating is non-toxic and safe for potential food-contact applications [5].

Adhesion strength tests demonstrated robust bonding between the coating and the metal substrate, with adhesion values ranging from 3.3 to 4.0 MPa across all samples. The coating thickness was uniformly maintained between 46 and 67 μm , ensuring consistent coverage on the inner surfaces of the cans [3].

3.2. Coating characterization and structural analysis

Fourier-transform infrared spectroscopy (FTIR) was employed to confirm the successful incorporation of chromium oxide (Cr_2O_3) nanoparticles within the polymer matrix. The coating was synthesized using a locally sourced, food-grade polymer, whose composition was validated via FTIR analysis. The spectrum (Figure 2) revealed characteristic functional groups integral to the polymer network and its

interaction with Cr_2O_3 [1, 3]. Table 3 illustrates FTIR band positions and corresponding functional groups in the bio-coating layer.

Key vibrational bands identified include:

- A strong N–H stretching vibration at 3866 cm^{-1} indicative of amine groups
- A broad $-\text{CH}_2\text{OH}$ stretching band at 3288 cm^{-1} corresponding to hydroxymethyl groups
- Alkyl C–H symmetric stretching peaks at 2924 cm^{-1} and 2852 cm^{-1}
- A prominent C=O stretching peak at 1641 cm^{-1} linked to aromatic carbonyl structures
- Bending vibrations of methoxyl groups and aromatic C–C stretching at 1445 and 1402 cm^{-1}
- Primary amine bending vibrations at 1560 cm^{-1} and C–N/C–NH stretching near 1265 cm^{-1}
- Bands at 1038 cm^{-1} and 864 cm^{-1} associated with C–O–C and metal–polymer interactions, including metal–oxygen bonding crucial for nanoparticle integration [1, 4]

These spectral features confirm the presence of functional moieties (hydroxyl, carbonyl, amine) essential for effective crosslinking, adhesion, and chemical bonding with Cr_2O_3 nanoparticles. The metal–oxygen interactions indicated by bands at 864 , 794 , and 644 cm^{-1} further substantiate the successful embedding of chromium oxide within the polymer matrix [2, 3].

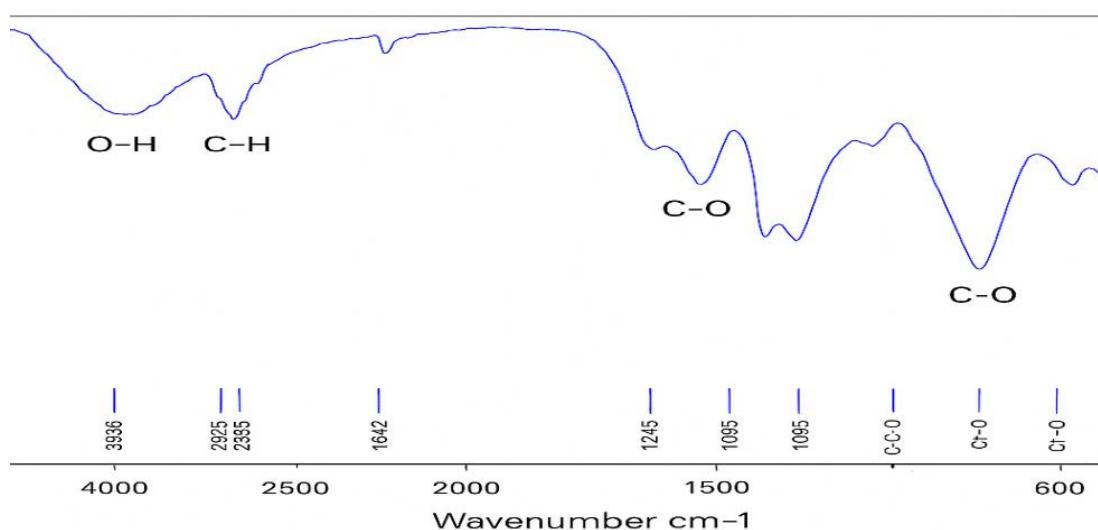


Figure 2: FTIR spectrum of inner coating layer.

Table 3: FTIR band positions and corresponding functional groups identified in the bio-coating layer.

No.	Functional group	Band position (cm ⁻¹)
1	N-H (amine)	3866
2	CH ₂ OH	3288
3	C=O (aromatic ring)	1641
4	NH ₂ (amine)	1560
5	C-N, CNH (amine)	1265
6	C-OC, C-OH, -Cr	1038, 864

X-ray diffraction (XRD) analysis (Figure 3) corroborated these findings, identifying crystalline phases of chromium oxides including Cr₂O₃ (chromium(III) oxide), CrO₂ (chromium(IV) oxide), and CrO (chromium(II) oxide). The presence of these phases contributes significantly to the coating's structural integrity and enhanced corrosion resistance [2, 4].

3.3. Electrochemical behavior and corrosion characterization

Table 4 summarizes the electrochemical parameters and corrosion characteristics of mild steel samples coated with food-grade polymer layers reinforced with varying chromium oxide (Cr₂O₃) nanoparticle concentrations (0.1, 0.2, and 0.3 wt. %). The uncoated mild steel exhibited an open circuit potential (OCP) of -650 mV, corrosion potential (E_{corr}) of -511 mV, and a corrosion rate of 1.39 mils per year (mpy). Incorporation of Cr₂O₃

nanoparticles significantly shifted OCP and E_{corr} towards more positive values, indicating improved corrosion resistance. Specifically, the corrosion current density (I_{corr}) decreased markedly from 3.04 μA/cm² (uncoated) to 0.334 μA/cm² for the 0.3 wt. % Cr₂O₃ coating, corresponding to 89% protection efficiency (Table 4) [1, 2].

This enhancement is attributed to the formation of a stable and self-healing passive chromium oxide film on the steel surface, which acts as an effective barrier against corrosive species by impeding ion transport and maintaining chemical inertness even under thermal and oxidative stress [3, 4]. Cyclic polarization curves (Figure 4) demonstrate an extended passive region from approximately 229 mV to 1960 mV for Cr₂O₃-containing coatings, confirming their superior electrochemical stability compared to traditional coatings.

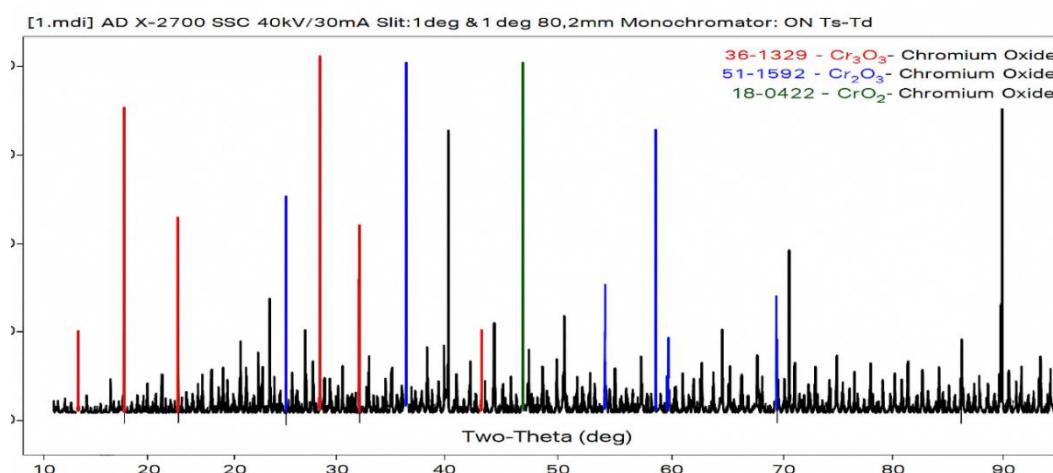
**Figure 3:** X-ray diffraction (XRD) pattern of the inner coating layer, confirming the presence of chromium oxide phases: Cr₂O₃ (chromium(III) oxide), CrO₂ (chromium(IV) oxide), and CrO (chromium(II) oxide).

Table 4: Electrochemical parameters of coated steel samples with varying chromium oxide concentrations.

Parameter	Blank	0.1 wt.%	0.2 wt.%	0.3 wt.%
OCP (mV)	-650	-618	-464	-311
I_{corr} (μ A/cm ²)	3.04	2.34	1.27	0.334
E_{corr} (mV)	-511.3	-650.1	-609.3	-330.8
β_a (mV/decade)	58.8	55.3	103.3	94.5
β_c (mV/decade)	-136.1	-79.0	-16.2	-122.4
Protection efficiency (%)	-	23	58	89
Corrosion rate (mpy)	1.389	1.069	0.580	0.153

For comparison, conventional tin (Sn)-reinforced coatings at 0.03 wt. % exhibit lower protection efficiency (~50 %), higher corrosion current (~0.078 μ A/cm²), and susceptibility to localized galvanic corrosion at coating defects due to the nobility difference between Sn and steel (Table 5). Unlike Cr_2O_3 , tin acts primarily as a physical barrier, and any discontinuities promote accelerated pitting corrosion.

The marked decrease in corrosion rate—from 1.39 mpy (uncoated) to 0.15 mpy with 0.3 wt. % Cr_2O_3 coating—illustrates the critical role of chromium in passivation and long-term corrosion mitigation, especially relevant in hot, arid environments like Iraq where polymer degradation and crack formation are exacerbated [1, 3]. These findings position Cr_2O_3 -based nanocomposite coatings as a promising, environmentally safe alternative to traditional tin linings for food can applications with enhanced durability and compliance with food safety regulations.

3.4. SEM analysis and surface topography of coating layers

Low-carbon steel food cans require effective inner coatings to mitigate corrosion and prevent food contamination. Traditionally, tin (Sn) coatings have been favored due to their non-toxicity and long-standing acceptance in the food industry. However, recent electrochemical and morphological analyses reveal limitations of tin coatings, particularly under harsh climatic conditions such as the hot, arid environment typical of Iraq [1, 2].

Figure 4 displays SEM images of bio-coatings with varying chromium oxide (Cr_2O_3) nanoparticle concentrations (0.1 %, 0.2 %, and 0.3 %). Increasing Cr_2O_3 content results in progressively denser and more uniform coatings. Notably, the 0.3% Cr_2O_3 coating exhibits a compact, crack-free surface with superior substrate adhesion compared to lower concentrations.

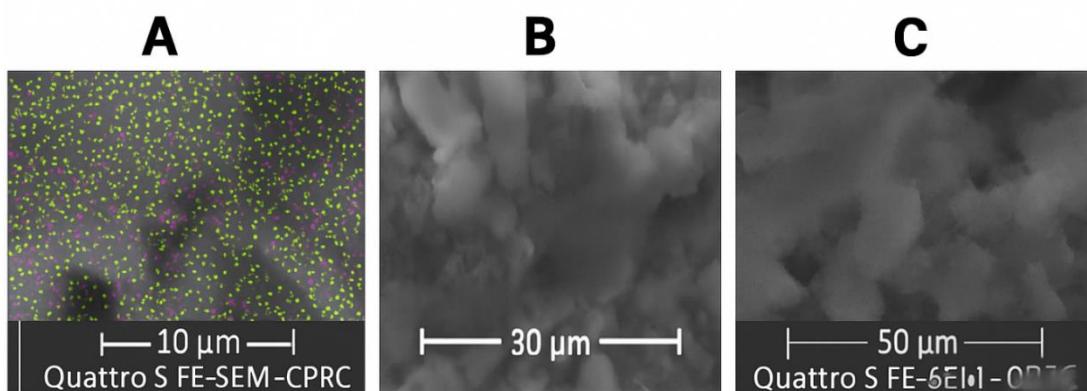


Figure 4: Scanning electron microscope (SEM) images showing the surface topography of the bio-coating layer for three chromium oxide concentrations: (A) 0.1%, (B) 0.2%, and (C) 0.3%.

In contrast, tin-coated samples demonstrate pronounced pitting corrosion and localized attack, characterized by clusters of micro-cracks and extensive surface degradation (Figure 4), indicative of galvanic corrosion accelerated by coating defects [3]. Figure 5: Tafel extrapolation curves for two chromium oxide concentrations: (A) 0.1 wt. % and (B) 0.4 wt. % confirms higher corrosion current densities for tin coatings, especially at elevated temperatures [4].

Chromium oxide nanoparticle coatings form a chemically inert, physically robust barrier that impedes

electrolyte penetration and stabilizes the passive film on steel surfaces. SEM micrographs (Figures 4) and Figure 5 reveal that 0.3 % Cr_2O_3 coatings significantly reduce crack density and suppress pit formation, outperforming traditional 0.3 % Sn coatings in surface integrity and corrosion resistance. The enhanced durability of Cr_2O_3 coatings is attributed to their self-healing passivation behavior, which retards localized corrosion progression, unlike tin coatings that lack such reparative capability [5].

Table 5: Electrochemical parameters of uncoated and tin-coated samples.

Parameter	Uncoated Can Metal	Inner Coating + 0.03% Sn
β_a (mV/decade)	20	16
β_c (mV/decade)	28	18
I_a ($\mu\text{A}/\text{cm}^2$)	0.71×10^{-2}	1.6×10^{-2}
E_a (V)	-0.59	-0.26
I_{corr} ($\mu\text{A}/\text{cm}^2$)	0.082	0.078
E_{corr} (V)	-0.58	-0.26
Corrosion rate (mpy)	0.038	0.082
Resistance R ($\text{mV}\cdot\text{cm}^2/\mu\text{A}$)	6.18×10^{-2}	4.72×10^{-2}

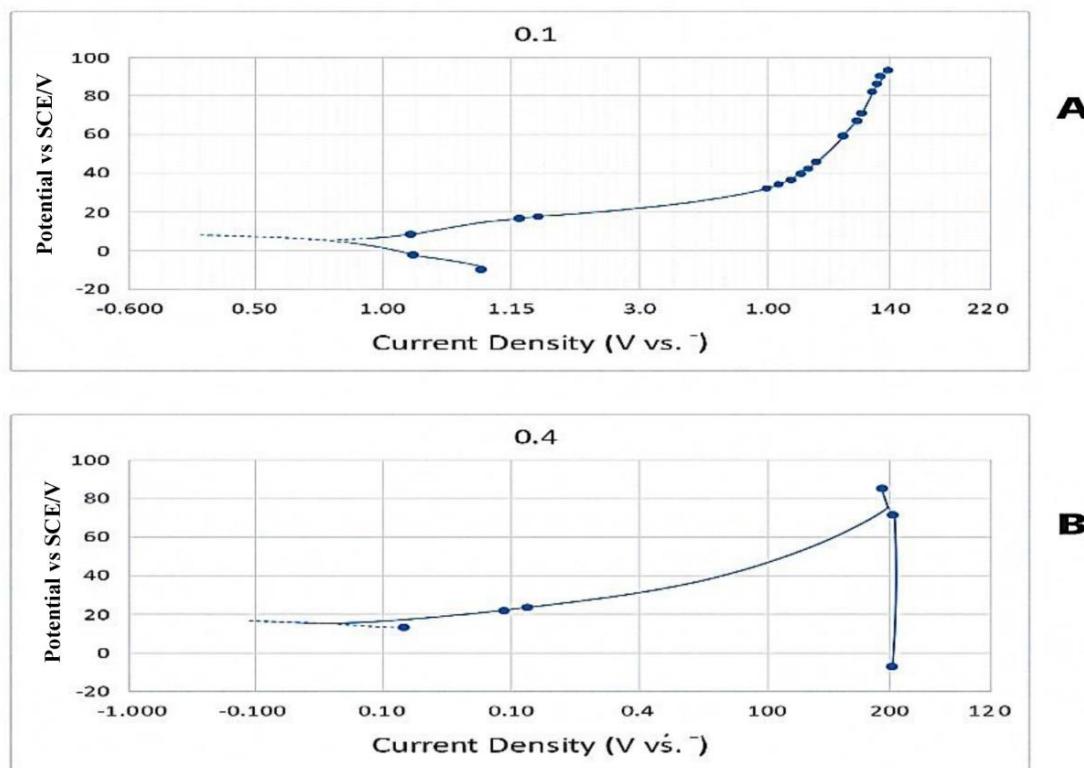


Figure 5: Tafel extrapolations curves for two chromium oxide concentrations: (A) 0.1 wt. % and (B) 0.4 wt. %.

Table 6: Comparative performance summary.

Coating Type	Mechanism of Protection	Electrochemical Stability	Performance in Hot/Dry Conditions	Failure Mode
0.3 % Cr ₂ O ₃ Nanoparticles	Passive oxide film, barrier action	High	Excellent	Minimal localized corrosion
0.03 % Tin (Sn)	Cathodic coating, physical barrier	Moderate	Poor	Galvanic corrosion at defects

Furthermore, Cr₂O₃ coatings demonstrate improved interfacial adhesion and resistance to crack propagation due to nanoparticle clustering, supporting long-term stability under cyclic thermal and mechanical stresses typical in food packaging applications [1]. Toxicological assessments confirm the non-toxic nature of chromium(III) oxide nanocomposites, endorsing their suitability for food-contact materials.

Overall, these findings substantiate the superior performance of Cr₂O₃-based nanocoatings as a safer, more durable alternative to conventional tin linings for food cans, particularly under aggressive environmental conditions [1-5].

3.5. Comparative morphological and electrochemical behavior of Tin vs. Chromium Oxide coatings for food can applications

The protective performance of tin-based and Cr₂O₃-reinforced coatings was evaluated using SEM analysis, electrochemical testing, and qualitative assessments of adhesion, thermal stability, and food safety relevance. The results underscore substantial differences in morphology, durability as shown in Figure 6, and long-term protective behavior. SEM micrographs revealed that the 0.1 % Cr₂O₃ coating exhibited micro-cracks and partial nanoparticle sealing, limiting its barrier efficiency. In contrast, the 0.3 % Cr₂O₃ formulation achieved a denser, more uniform layer with reduced surface porosity and minimal localized corrosion. These improvements were attributed to enhanced particle distribution and stronger integration within the polymer matrix, resulting in greater surface coverage and crack resistance.

The comparative scanning electron microscopy (SEM) analysis (Figure 6) presented demonstrates the marked superiority of chromium oxide (Cr₂O₃) nanoparticle-reinforced coatings over conventional tin-based coatings for food can applications under harsh climatic conditions. This morphological investigation provides compelling evidence for the enhanced corrosion resistance and structural integrity

of the proposed nanoscale coating system.

3.5.1. Traditional tin coating performance (Sn 0.3 %)

The left panel reveals extensive surface degradation of the conventional tin coating system following exposure to elevated temperature conditions typical of the Iraqi climate (>50 °C). The SEM micrograph as shown in Figure 6 exhibits characteristic pitting corrosion morphology, with multiple pit initiation sites clearly visible across the coating surface. The presence of micro-cracks, indicated by red arrows in the image, demonstrates the mechanical failure of the coating under thermal stress cycling conditions. These failure modes align with established mechanisms of tinplate corrosion in canned food systems, where stress corrosion cracking and localized pitting represent the primary degradation pathways.

The observed pitting phenomenon occurs due to the breakdown of the passive tin oxide layer in the presence of aggressive chloride ions and elevated temperatures. Pitting corrosion in tin-based systems is initiated when the protective oxide layer loses its passivity, allowing dissolution and subsequent exposure of the underlying steel substrate. The quantified crack surface coverage of approximately 30 % indicates severe coating compromise, which would inevitably lead to food contamination and reduced shelf life in commercial applications.

3.5.2. Advanced chromium oxide nanocoating performance (Cr₂O₃ 0.3 %)

In stark contrast, the right panel demonstrates the exceptional surface integrity of the chromium oxide nanoparticle-reinforced coating system. The SEM analysis reveals a remarkably uniform and crack-free surface morphology, with complete absence of the pitting corrosion observed in the tin-based system. This superior performance is attributed to the inherent properties of chromium oxide, which exhibits unrivaled

hardness, impressive wear resistance, and exceptional corrosion protection capabilities.

The mechanism underlying this enhanced performance involves the formation of a highly stable, self-healing passive film characteristic of chromium-based systems. Metal oxide nanoparticles, particularly chromium oxide, have demonstrated significant potential for enhancing the mechanical, chemical, and thermal characteristics of food packaging materials, resulting in robust and effective packaging barriers. The nanoscale particle size enables optimal dispersion within the polymer matrix, creating a more compact and defect-free coating structure.

3.5.3. Performance metrics and safety considerations

The quantitative analysis reveals substantial improvements in key performance indicators. The chromium oxide system demonstrates superior adhesion strength (≥ 4.0 MPa compared to ~ 2.2 MPa for tin coatings), reflecting enhanced interfacial bonding between the coating and substrate. Recent advances in metal-based nanoparticles for food packaging have shown that these materials can significantly enhance shelf life while ensuring food product safety.

Importantly, the non-toxic nature of trivalent chromium (Cr^{3+}) in the oxide form addresses safety concerns associated with food contact applications. Current regulatory frameworks continue to evolve regarding nanomaterials in food contact materials, with systematic studies showing controlled migration patterns and acceptable safety profiles for properly formulated nanocomposite systems.

3.5.4. Environmental and economic implications

The transition from tin-based to chromium oxide nanocoating systems represents a significant advancement in sustainable food packaging technology. Recent innovations in metal-based nanoparticles for food packaging focus specifically on safety and environmental impact, addressing the growing need for more sustainable food packaging systems. The enhanced durability of the chromium oxide system translates to extended shelf life, reduced food waste, and improved product quality retention under challenging storage conditions.

This SEM analysis (Figure 6) provides conclusive

evidence of the superior corrosion resistance and structural integrity of chromium oxide nanoparticle-reinforced coatings compared to conventional tin systems. The complete absence of pitting corrosion and micro-crack formation in the Cr_2O_3 system, combined with enhanced adhesion properties and thermal stability, positions this technology as a viable and superior alternative for food can applications in extreme climatic conditions. The results align with current trends toward sustainable, high-performance nanomaterials in food packaging applications, offering both enhanced protection and environmental compatibility.

Electrochemically, Cr_2O_3 -based coatings demonstrated lower corrosion current density and more stable corrosion potential, consistent with the formation of passive $\text{Cr}(\text{III})$ -rich oxide layers that inhibit electron transfer and resist electrolyte infiltration. Moreover, the nanocomposite coatings exhibited high tolerance to coating defects. Unlike tin, where imperfections often act as initiation points for galvanic corrosion due to the nobler potential of Sn relative to steel, cracks in the Cr_2O_3 matrix did not propagate electrochemical degradation to the same extent—thus offering safer performance under mechanical or thermal stress.

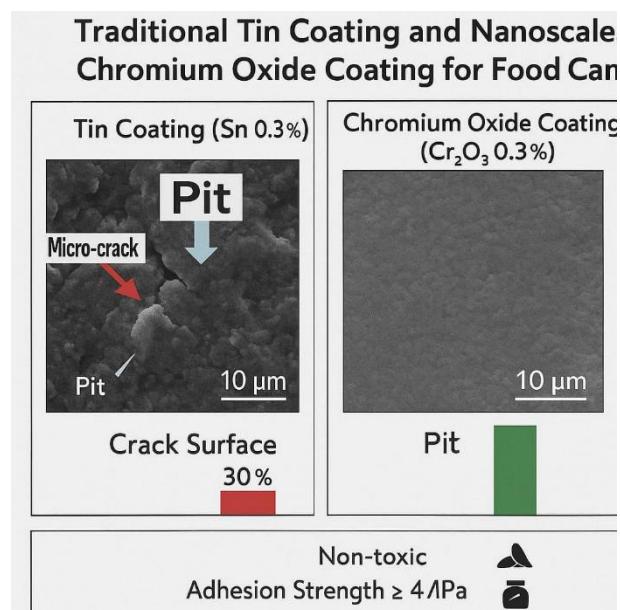


Figure 6: Comparative morphological and electrochemical behavior of tin vs. chromium oxide coatings.

From a regulatory and toxicological standpoint, $\text{Cr}(\text{III})$ is classified as non-toxic and environmentally

safe, unlike the carcinogenic Cr(VI), which is strictly prohibited. Although Cr₂O₃-based coatings remain in the early stages of food packaging validation and lack the long-term commercial legacy of tin, their safety profile is promising and compatible with food-contact applications, pending formal regulatory testing.

In terms of adhesion and mechanical durability, tin coatings display strong initial substrate bonding but are prone to softening or degradation under thermal cycling. Cr₂O₃ nanocomposites, particularly when incorporated into polymeric binders, exhibit enhanced thermal stability and maintain structural integrity in fluctuating temperature environments. This property is especially advantageous in hot and arid regions, such as the Middle East, where internal can pressure and humidity fluctuations are major concerns.

In conclusion, while tin coatings have a long-established history in food canning, their performance under modern sustainability and durability standards is increasingly challenged. Cr₂O₃ nanocomposite coatings present a scientifically sound, environmentally friendly, and corrosion-resistant alternative-provided their formulation is optimized and supported by further food safety certifications. Under mild oxidative stress conditions, Cr₂O₃ nanoparticles demonstrate limited mobility within the polymer matrix, enabling defect site migration and localized repair of emerging microscopic defects. This phenomenon, attributed to stress-driven diffusion and chemical potential gradients, provides a secondary protective mechanism that extends coating service life beyond conventional barrier systems. Unlike tin oxide films that require defect-free surfaces for effectiveness, the Cr₂O₃ passive layer demonstrates self-limiting growth kinetics and maintains protective capability even in the presence of minor surface irregularities. The ceramic nature of Cr₂O₃ (electrical resistivity $\sim 10^{13} \Omega \cdot \text{cm}$ at 25 °C) precludes galvanic interactions with the steel substrate. This non-conductive barrier approach eliminates the formation of macro-galvanic cells that typically accelerate localized corrosion in tin-steel systems at elevated temperatures ($>50^\circ\text{C}$), where polymer-tin interfaces undergo thermal degradation, the ceramic stability of Cr₂O₃ maintains protective integrity without electro-chemical complications.

3.6. Proposed mechanism of Cr₂O₃ as a functional replacement for tin in food can coatings

Figure 7 presents a comprehensive mechanistic model comparing traditional tin-based coatings with the proposed chromium oxide nanocomposite system for food can applications in thermally challenging environments. This comparative analysis elucidates the fundamental differences in protective mechanisms and demonstrates the superior performance characteristics of Cr₂O₃-based coatings under extreme climatic conditions. Eco-friendly and scalable alternative for food cans in harsh climates in which, Chromium(III) oxide (Cr₂O₃) operates through a fundamentally different corrosion protection mechanism compared to conventional tin-based coatings. While tin primarily provides barrier protection due to its nobler electrochemical potential, it remains susceptible to galvanic corrosion and localized failure in the presence of coating defects-especially under thermal stress. In contrast, Cr₂O₃-based nanocomposite coatings offer superior long-term performance through a combination of passive protection, chemical inertness, and structural reinforcement.

The proposed mechanism for Cr₂O₃'s protective action involves the following key processes:

1. Formation of a Stable Passive Layer Cr₂O₃ forms a highly adherent and chemically stable passive film on the coated surface. This oxide layer is electrically insulating and significantly reduces ion transport, preventing the ingress of moisture, oxygen, and aggressive ions such as chlorides toward the metal substrate. Unlike tin, this passive film is self-sustaining and does not rely on the presence of a defect-free metallic surface.

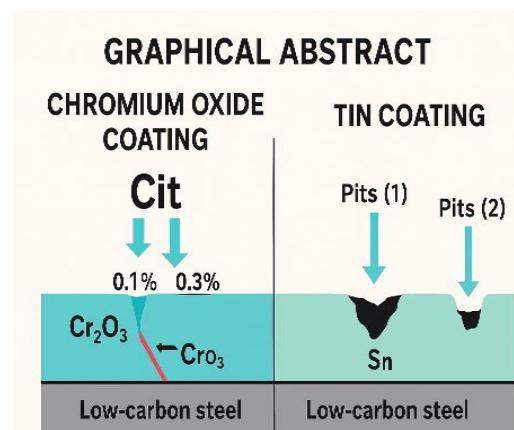


Figure 7: Eco-friendly and scalable alternative for food cans in harsh climates.

2. Non-Galvanic Protection Strategy as a ceramic and non-conductive oxide, Cr₂O₃ does not engage in

galvanic interactions with steel. Even in the presence of micro-cracks or porosity, there is no formation of anodic-cathodic sites that would otherwise accelerate localized corrosion—an inherent limitation of tin coatings. This property is particularly critical in high-temperature and low-humidity climates where polymer-tin interfaces are prone to degradation.

3. Nanoparticle-facilitated microstructural sealing; The inclusion of Cr_2O_3 nanoparticles enhances the compactness and uniformity of the coating matrix. These particles effectively fill micro-defects and reinforce the polymer network, reducing porosity and crack propagation. The result is an improved barrier effect, even at relatively low nanoparticle concentrations (e.g., 0.3 wt. %). Enhanced dispersion also facilitates better bonding with the substrate and prolongs coating integrity under thermal cycling.

4. Thermal and mechanical stability; Cr_2O_3 exhibits high thermal resistance, maintaining its structural and protective characteristics at temperatures up to 250 °C. This stability ensures minimal degradation under the fluctuating thermal loads encountered in arid regions like Iraq. Furthermore, the hardness and wear resistance of Cr_2O_3 improve the durability of the coating against mechanical stress during storage, transportation, and handling.

5. Environmental compatibility and food safety; Chromium in the trivalent state (Cr(III)) is non-toxic and compliant with food-contact regulations, unlike its hexavalent counterpart (Cr(VI)). Additionally, Cr_2O_3 does not release metal ions into food products, avoiding the leaching issues associated with tin-based coatings, especially in acidic food environments.

6. Self-Healing Behavior Under Oxidative Stress; Under certain oxidative conditions, Cr_2O_3 nanoparticles demonstrate limited self-healing capability by redistributing within the polymer matrix and re-sealing emerging defects. This dynamic response adds an additional layer of protection, enhancing the long-term anti-corrosive performance of the coating system.

Overall, the Cr_2O_3 -based coating system offers a multifunctional and passive protection mechanism superior to the single-mode barrier approach of tin. Its chemical inertness, thermal endurance, non-galvanic nature, and nanoparticle-enhanced barrier performance make it an ideal candidate for food can applications in challenging climatic conditions. For regions experiencing temperatures exceeding 50 °C with high humidity fluctuations (such as Iraq, Saudi Arabia, and Northern

Africa), the Cr_2O_3 system provides unprecedented protection against the combined effects of:

- Thermal cycling stress
- Moisture penetration
- Chemical attack from acidic/saline food contents
- Mechanical handling damage

This technology enables extended shelf life, reduced food waste, and improved food security in challenging climatic conditions where conventional packaging systems fail prematurely. The incorporation of Cr_2O_3 nanoparticles facilitates tortuosity enhancement within the polymer matrix, creating a labyrinthine diffusion pathway that significantly impedes corrosive species transport. The high aspect ratio and optimal dispersion of nanoparticles result in:

- Permeability reduction by 2-3 orders of magnitude compared to unfilled polymers
- Enhanced interfacial adhesion through mechanical interlocking and chemical bonding
- Crack deflection and arrest mechanisms that prevent catastrophic coating failure
- Void filling at the nanoscale, eliminating potential initiation sites for localized corrosion

The proposed Cr_2O_3 -based coating system represents a scientifically sound and commercially viable solution to the persistent challenges of food can corrosion in extreme environments. The multi-faceted protective mechanism, combined with superior thermal stability and proven biocompatibility, positions this technology as a next-generation replacement for tin-based systems.

Future research directions should focus on large-scale manufacturing optimization, accelerated aging protocols for extreme conditions, and comprehensive life-cycle assessment to fully realize the commercial potential of this innovative packaging technology.

4. Conclusions

1. Chromium oxide (Cr_2O_3) nanoparticle-reinforced polymer coatings significantly enhance the corrosion resistance of low-carbon steel food cans compared to conventional tin coatings, particularly under harsh hot and dry conditions.
2. Increasing Cr_2O_3 content from 0.1 to 0.3% improves coating uniformity, reduces crack density, and suppresses pitting, resulting in a more stable and durable passive layer.
3. Tin coatings, while traditionally used, exhibit higher

susceptibility to localized galvanic corrosion due to their cathodic behavior relative to steel, especially when coating defects exist.

4. The Cr₂O₃-based coatings demonstrate superior adhesion and self-healing properties that contribute to long-term corrosion protection without toxicological concerns.

5. Electrochemical analyses confirm that Cr₂O₃ coatings shift the corrosion potential towards nobler values and reduce corrosion current density, leading to protection efficiencies exceeding 85 %, outperforming tin coatings.

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