Antioxidant capacity of biopolymer films reinforced with green Carbon Dots as active protection for oil-based products

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The oxidation process of oil-based products supposes a devaluation of quality and inherent properties of edible oils and oils with industrial applications, so their useful life is reduced. From an economic point of view, the deterioration of oil-based products has a significant negative impact on industries. For this reason, the development of **sustainable active packaging** for this type of product has gained interest in the last few years.

Within this context, we study the antioxidant properties of **bio-polymer-based films (BPFs)** obtained from high methoxylated pectin **(HMP)** and sodium caseinate **(CAS)**. The addition of carbon nanoparticles, like Carbon Dots (CDs), as biofilm reinforcement has benefits on food preservation due to their antioxidant properties. Furthermore, CDs show high biocompatibility and low toxicity so they are not a potential risk to human health.

In this work, **green Carbon Dots (gCDs)** obtained from natural sources like rosemary powder (RCDs) and apple pomace (APCDs) were incorporated in CAS-HMP initial suspension at different concentrations (0.25%, 0.5% and 1%) as active agents. The antioxidant capacity of BPFs reinforced with both types of gCDs was evaluated by the DPPH assay and peroxide value (PV) method. AFM studies were carried out to determine biofilm surface roughness depending on the type and concentration of gCDs used. ELS measurements provide information about the surface charge of nanoparticles and their colloidal stability. Finally, stability studies based on the intrinsic fluorescence signal of oil and gCDs demonstrate that gCDs are not released from the film due to their low dispersibility in the hydrophobic medium.

Preparation of bio-films enriched with antioxidant gCDs


Rosemary powder

or


Apple pomace powder

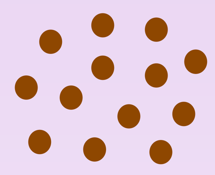
+ ultrapure water

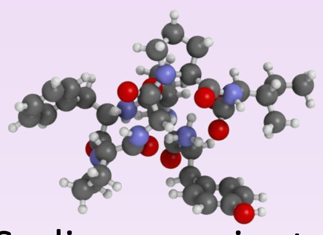
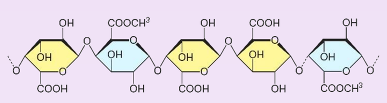
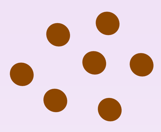

200 ºC, 5 h
+ 5 mL water added every 30 min

Centrifugation
12,000 rpm, 50 min
+
Dialysis
MWCO 5 kDa, 1 h


gCDs suspension

Freeze-drying


gCDs powder


Sodium caseinate suspension
+

High-methoxylated pectin suspension
+

0.25, 0.5 or 1% gCDs
+
Glycerol (plasticizer)

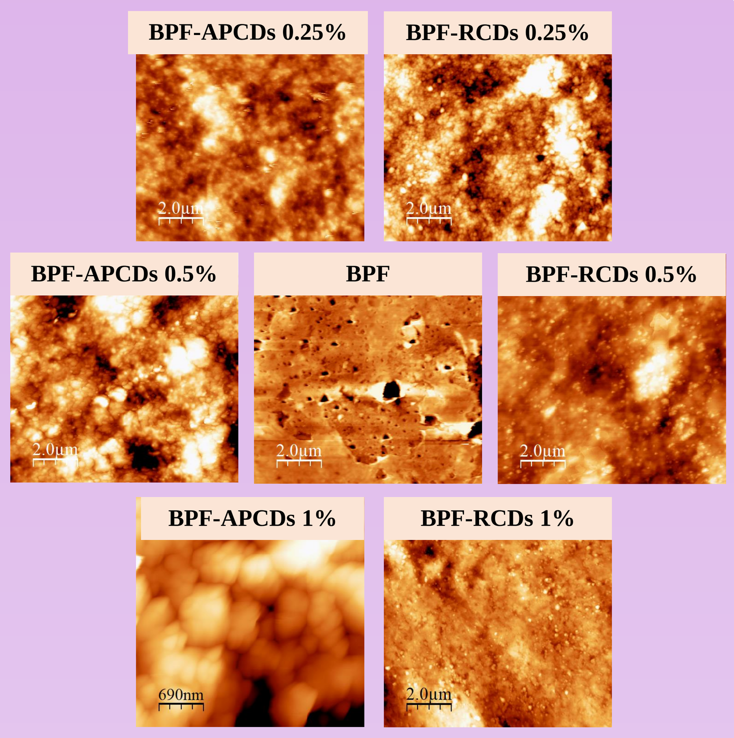

Petri dish
Dried for 24 h, 40 ºC

Bio-films enriched with gCDs

Biofilms characterization

AFM images: surface roughness

Sample	Average roughness (nm)
BPF	12.4
RCD-BPF 0.25%	10.6
RCD-BPF 0.5%	10.0
RCD-BPF 1%	8.1
APCD-BPF 0.25%	10.0
APCD-BPF 0.5%	14.1
APCD-BPF 1%	93.9



· Roughness values are lower in RCD-BPFs, independently of their concentration

· Higher concentrations of APCDs raised roughness values → Formation of agglomerates

The presence of CDs into the BPFs matrix modifies its structure, filling the pores initially observed

ELS measurements: colloidal stability of gCDs

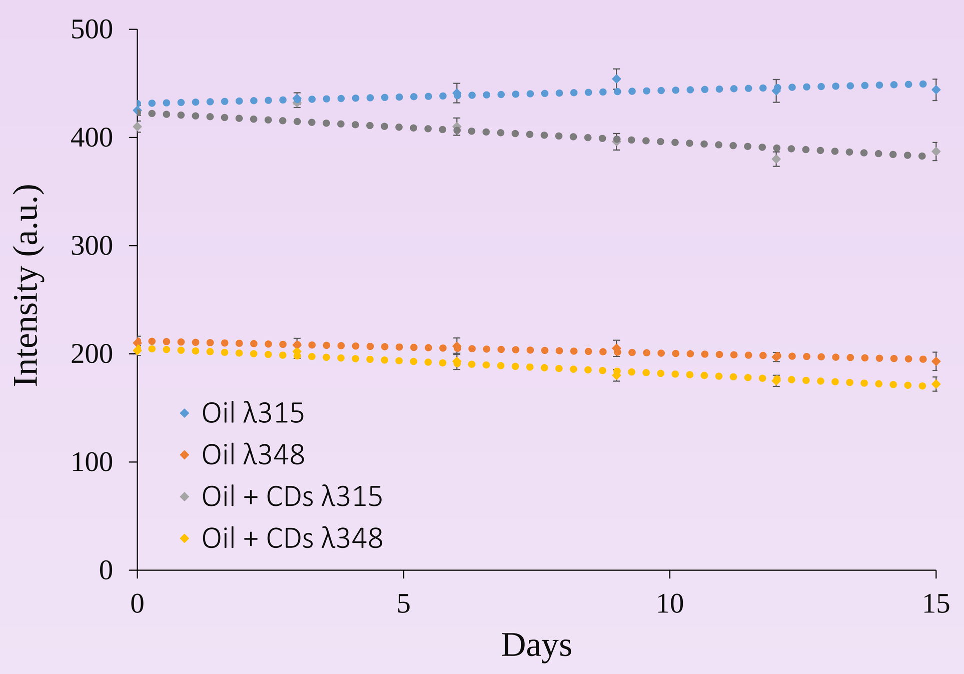
Sample	ζ-potential (mV)
RCDs	-13 ± 2
APCDs	-4 ± 1

ζ-potential values lower than ± 10 mV indicate that dispersions are highly unstable, leading to flocculation processes

Stability studies: intrinsic fluorescence signal

Are gCDs leaching from the films towards the oily sample?

λ_{exc} (oil) = 315 nm
λ_{exc} (gCDs) = 348 nm



The emission intensity of the oil without gCDs remained statistically constant over time

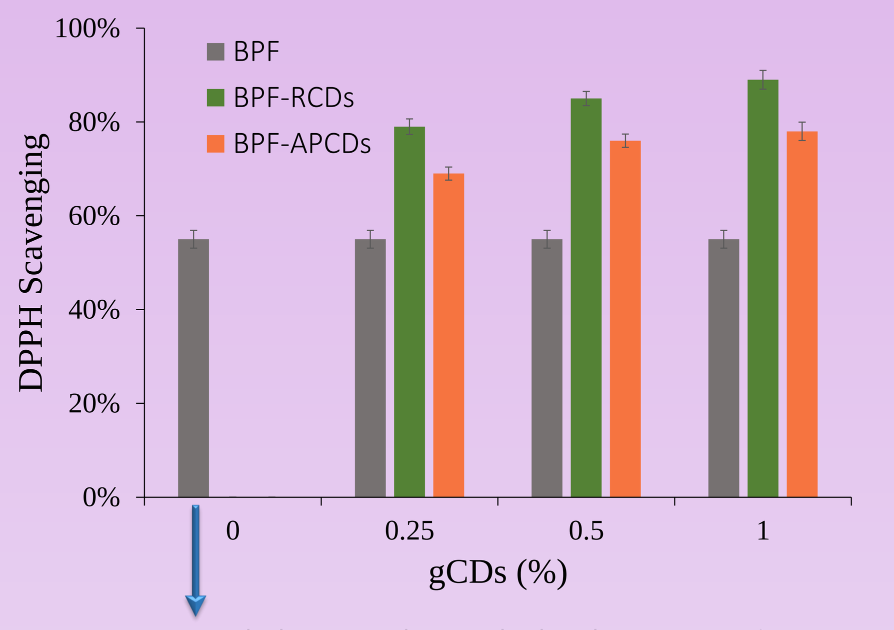
Emission of the oil containing gCDs –BPFs decreases slightly due to the relative humidity of the biofilms

Low traces of water could be released forming reverse micelles and modifying the polarity of the medium

gCDs are not released from the film due to the hydrophobic nature of the medium and the low dispersibility of the nanoparticles in it

Antioxidant capacity

DPPH free radical scavenging assay



BPFs exhibit a relatively high antioxidant activity itself: 55% inhibition of DPPH·

DPPH methanolic solution
+
increasing CDs concentrations

30 min of incubation
(darkness, room temperature)

Absorbance measurement at 517 nm

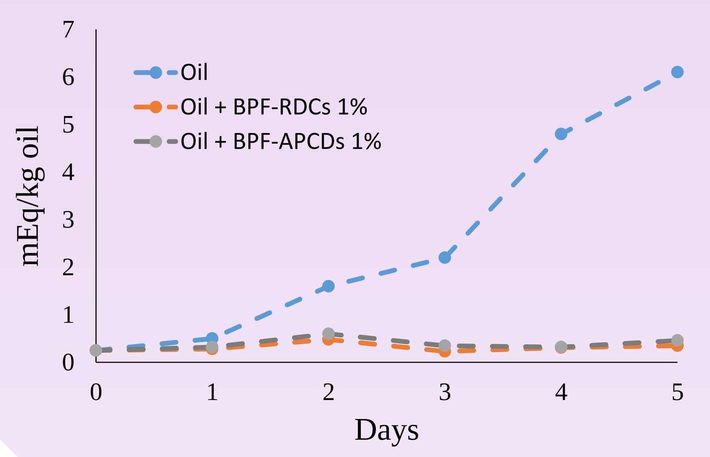
$$\% \, Inhibition = \left[100 - \frac{A_{s+DPPH} - As}{A_b}\right] \cdot 100$$

A_{s+DPPH}: Abs sample (gCDs) + DPPH
A_s: Abs sample (gCDs)
A_b: Abs blank (DPPH)

RCDs-BPFs present higher antioxidant activity than APCDs-BPFs for each concentration evaluated

Peroxide Value (PV) method

Oil sample dissolved in Cl_3CH/glacial acetic acid mixture + KI aqueous solution + sodium thiosulfate → **Iodometric titration** by potentiometric determination



$$PV = \frac{(V - Vo) \cdot Ct \cdot 1000}{w}$$

V, V_o: volumes of the sodium thiosulfate added to the oil sample and blank solution
C_t: molar concentration of sodium thiosulfate
w: weight of the oil sample

PV remained at a low value throughout the study time, indicating that the 1% gCD-BPFs stabilized the oil due to the consumption of the peroxides generated

FINAL REMARKS

✓ Bio-polymer-based films for **sustainable active packaging** were successfully synthesized from high methoxylated pectin and sodium caseinate.

✓ The reinforcement with antioxidant gCDs demonstrated advantages to **prevent the deterioration of oil-based products** due to the antioxidant properties of this type of nanomaterials.

✓ The addition of RCDs to BPFs resulted in more homogeneous and less rough films in comparison to APCDs-BPFs. In addition, antioxidant properties are higher for RCDs-BPFs, so CDs obtained from rosemary seem to be the best option to reinforce biofilms.

References

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