Escuela Superior Politécnica del Litoral

Caractérisation de propriétés thermiques, mécaniques et antimicrobiennes des films actifs de PLA et d'huile essentielle d'origan traités par plasma froid

Rómulo Salazar[1]*, Wilfrido Terán-Verzola[1], Ximena Yépez[1], Veronica Salas-Gomez[1], Sandra Domenek[2]

[1]Escuela Superior Politécnica del Litoral, ESPOL, Facultad de Ingeniería en Mecánica y Ciencias de la Producción, Guayaquil, Ecuador.

[2]Université Paris-Saclay, INRAE, AgroParisTech, UMR SayFood, Palaiseau, France.

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Introduction

Plastics Pollution

Between 1950 and 2015, approximately 8.3 billion tons of plastics were produced, of which **6.3 billion tons are considered waste** (Geyer, Jambeck & Law, 2017).

SCIENCE ADVANCES | RESEARCH ARTICLE

PLASTICS

Production, use, and fate of all plastics ever made

Roland Geyer,[1]* Jenna R. Jambeck,[2] Kara Lavender Law[3]

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Plastics have outgrown most man-made materials and have long been under environmental scrutiny. However, robust global information, particularly about their end-of-life fate, is lacking. By identifying and synthesizing dispersed data on production, use, and end-of-life management of polymer resins, synthetic fibers, and additives, we present the first global analysis of all mass-produced plastics ever manufactured. We estimate that 8300 million metric tons (Mt) as of virgin plastics have been produced to date. As of 2015, approximately 6300 Mt of plastic waste had been generated, around 9% of which had been recycled, 12% was incinerated, and 79% was accumulated in landfills or the natural environment. If current production and waste management trends continue, roughly 12,000 Mt of plastic waste will be in landfills or in the natural environment by 2050.

INTRODUCTION

A world without plastics, or synthetic organic polymers, seems unimaginable today, yet their large-scale production and use only dates back to ~1950. Although the first synthetic plastics, such as Bakelite, appeared in the early 20th century, widespread use of plastics outside of the military did not occur until after World War II. The ensuing rapid growth in plastics production is extraordinary, surpassing most other man-made materials. Notable exceptions are materials that are used extensively in the construction sector, such as steel and cement (1, 2).

density polyethylene (PE), low-density and linear low-density PE, polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC), polyethylene terephthalate (PET), and PUR resins; and polyester, polyamide, and acrylic (PP&A) fibers. The pure polymer is mixed with additives to enhance the properties of the material.

RESULTS AND DISCUSSION

Global production of resins and fibers increased from 2 Mt in 1950 to 380 Mt in 2015, a compound annual growth rate (CAGR) of 8.4%

76% are considered waste

Biodegradable packaging

Polylactide (PLA)

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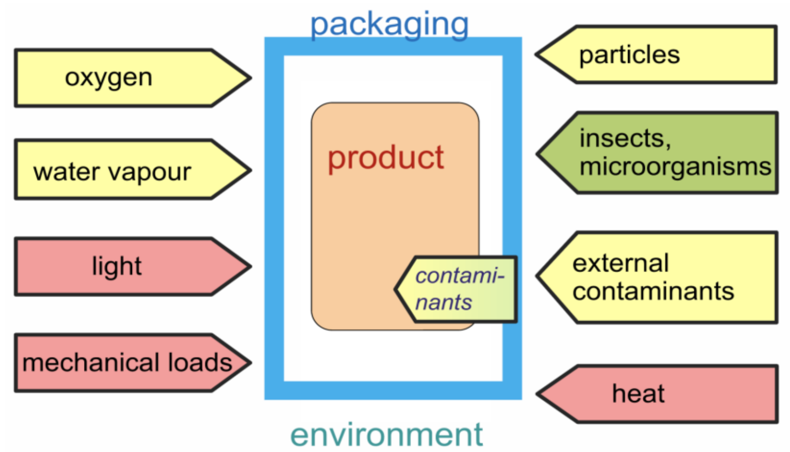
Introduction

Functions of food packaging

1. **Food safety**
   - Protect quality and safety
   - Reduce food losses



2. **Transport, containment, convenience**
3. **Communication and information of the consumer**
   - Legal information
   - Communication and counsel of the consumer
4. **Marketing**
5. **Environment** - decreasing ecological footprint the total service offer

Food loss and waste
930 millon Tons in 2019*

Active packaging

Using **essential oils (EOs)**** such as **oregano**

Advantages

- Antioxidant activity
- Antimicrobial activity
- Shelf-life improvement
- Possibility of reuising food waste as source of Eos

Disadvantages

- High volatility
- Low solubility (lipophility)
- Easy degradation

*United Natons Environment Programme (2021). Food Waste Index Report 2021

Carpena, M.; Nuñez-Estevez, B.; Soria-Lopez, A.; Garcia-Oliveira, P.; Prieto, M.A. *Resources* **2021, *10*, 7.

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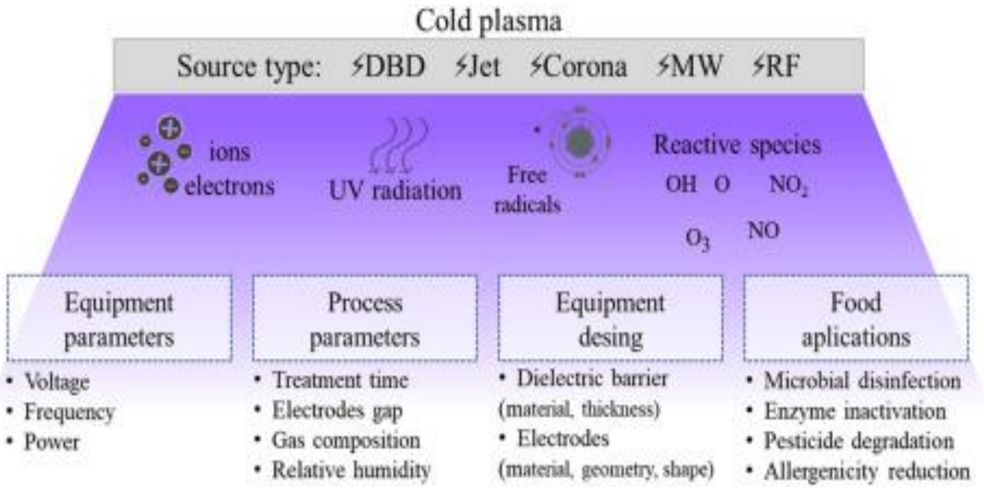
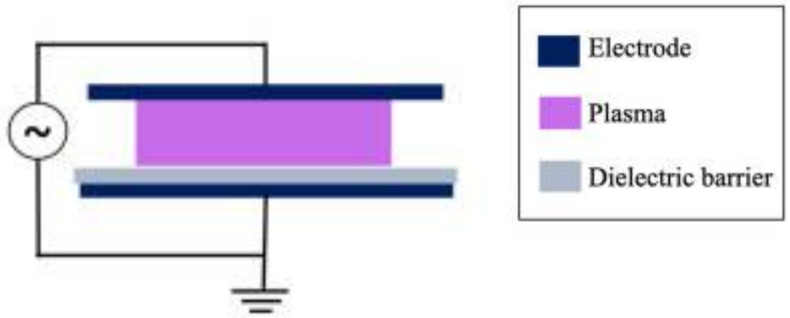
Introduction

Cold Plasma in food processing





Atmospheric pressure dielectric barrier discharges (DBD)

Cold plasma

- a non-thermal technology for food decontamination and chemical modification
- interaction of the plasma reactive species with the surface of food and materials
- method to improve the physical and chemical properties of polymers, including PLA**

No previous studies on PLA/OEO active packaging samples treated with Cold plasma

Do Cold plasma treatments have an impact on the sample properties?

*Figure from Laroque, D. A., Seó, S. T., Valencia, G. A., Laurindo, J. B., & Carciofi, B. A. M. (2022). *J. of Food Engineering, 312, 110748.*

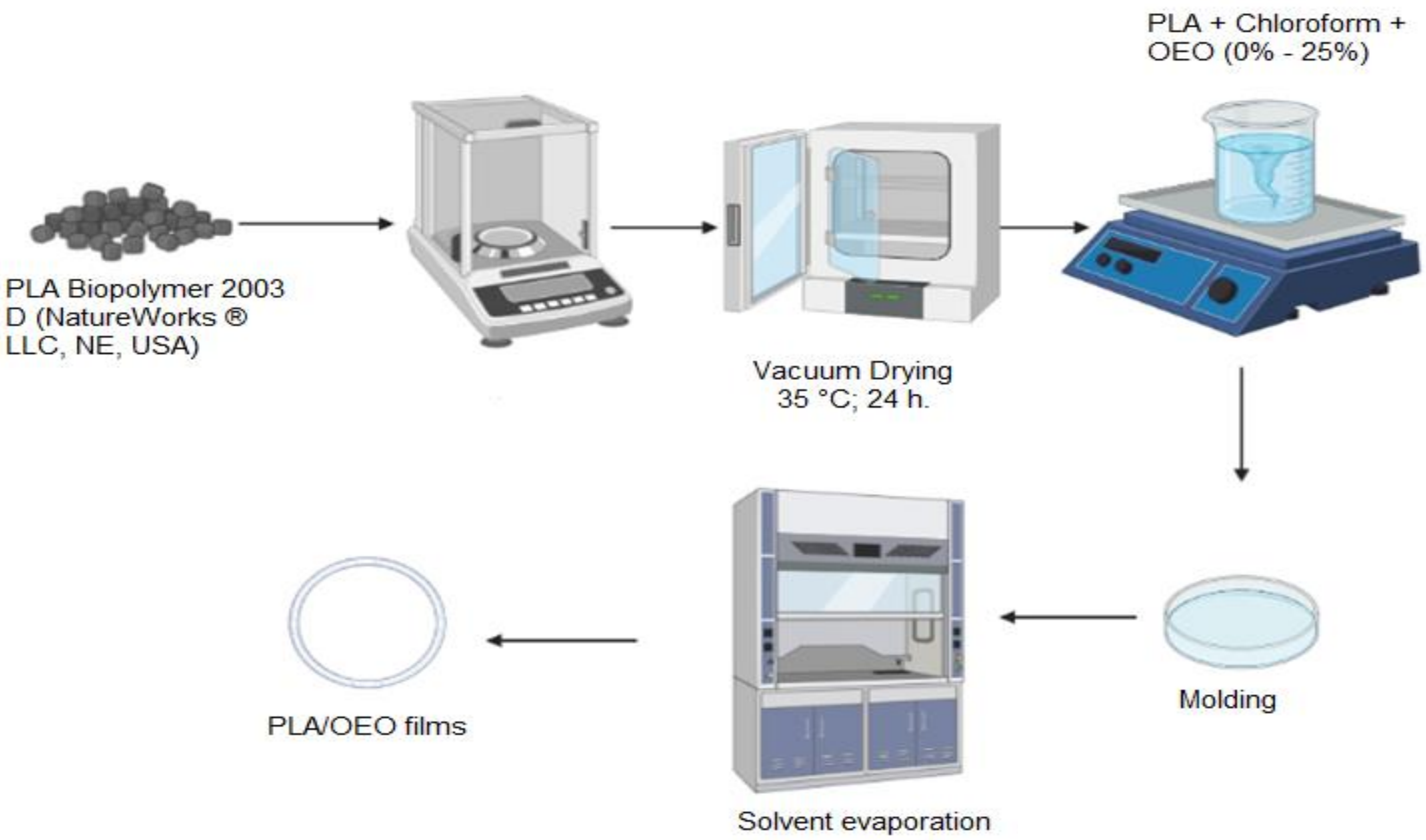
**Perera, Kalpani Y., Jack Prendeville, Amit K. Jaiswal, and Swarna Jaiswal. 2022. Coatings 12(12):1–19.

Materials and Methods

PLA 2003D
(NatureWorks)
4 – 4.5% of D-Lactic acid

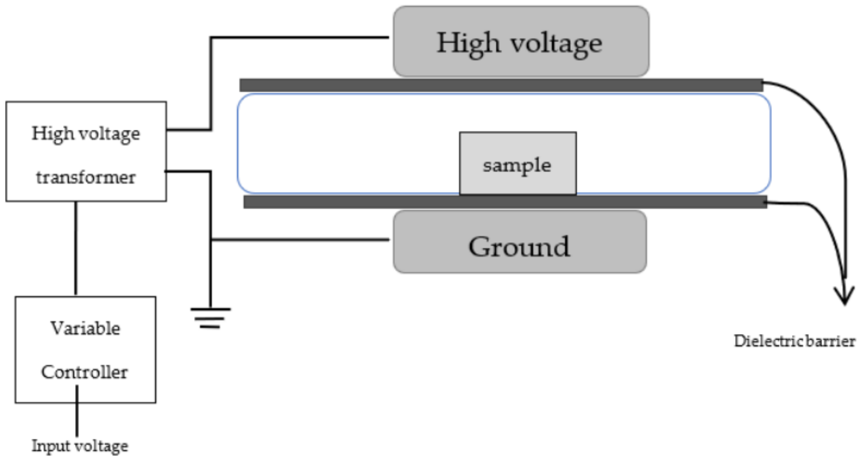
Oregano Essential Oil
(NOW, IL, USA)
~ 67 % Carvacrol
~ 11 % Cymene

Preparation of films by Solvent Casting Method



Materials and Methods

Cold Plasma Treatment



Parameter	0 min	15 min
Voltage (kV)	-	89 ± 1.5
Current (mA)	-	0.49 ± 0.03
Temperature top electrode (°C)	29.1 ± 1.5[a]	31.4 ± 0.3[a]
Temperature bottom electrode (°C)	30.2 ± 2.5[a]	33.3 ± 0.8[a]
Laboratory temperature (°C)	23.7 ± 0.9[a]	22.6 ± 0.4[a]
Laboratory humedity (%)	43.3 ± 2.2[a]	41.3 ± 0.2[a]
Sample temperatura (°C)	23.3 ± 0.9[a]	34.7 ± 1.4[b]

Atmosphere: Air and Nitrogen
Conditions: 90 kv during 15 min

Cold Plasma Lab - ESPOL

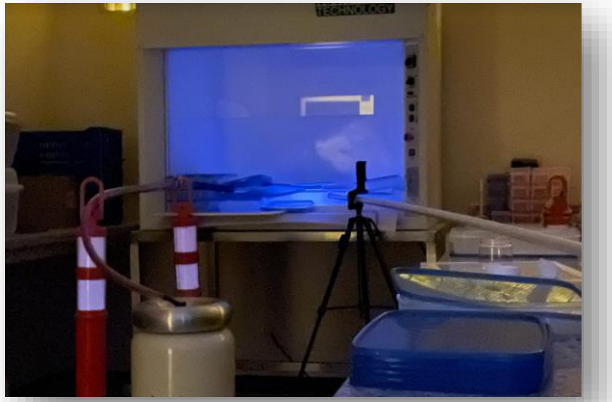


Figure from: Mahanta, S., Habib, M. R., & Moore, J. M. (2022). *International Journal of Molecular Sciences*, *23*, 1611 espol Escuela Superior Politécnica del Litoral

Materials and Methods

Coding of the PLA samples

Code	OEO	Cold Plasma with Nitrogen	Cold Plasma with Air
PLA	-	-	-
P25	25%	-	-
P-CPA	-	-	+
P-CPN	-	+	-
P25-CPA	25%	-	+
P25-CPN	25%	+	-

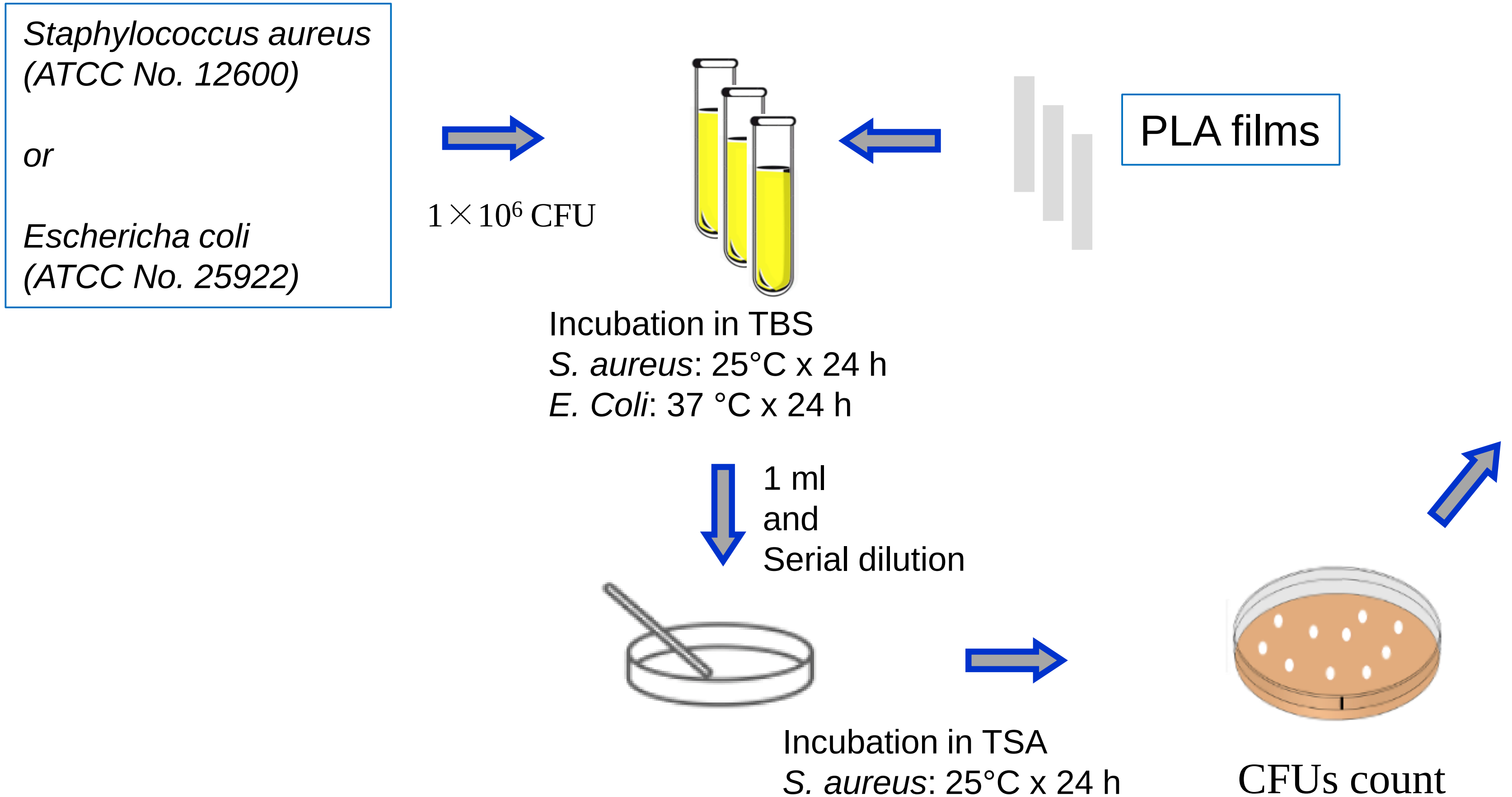
Thermal and mechanical properties

Thermal Analysis SDT Q200
10 ºC/min from -30 to 200 ºC, with double scanning

Shimadzu® UTM-600KN according to the ASTM D-882 at a rate of 5 mm/min

Materials and Methods

Anticrobial properties*



R = log (B/A)

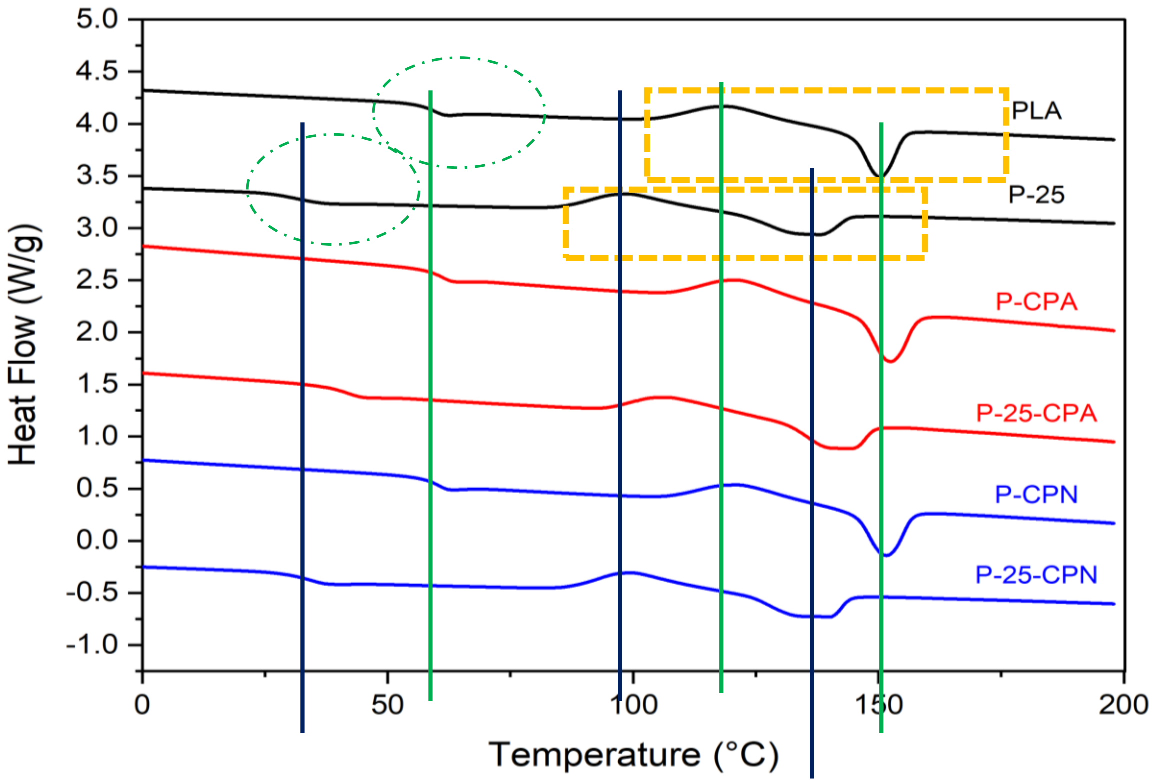
where:

R is quantitative reduction in bacteria,
A is the average number of viable cells on the test sample and,
B is the average number of viable cells on control sample.

*Salazar, R., Salas-Gomez, V., Alvarado, A., and Baykara H. 2022. *Polymers* 14(11):2266

Results

Thermal properties: DSC



Plasticizing effect due to the incorporation of oregano essential oil (phenolic compounds: carvacrol), similar to effect of benzaldehyde already reported in PLA films*

The Tc and Tf decrease in PLA/OEO films due to the molecular structure of the OEO components that can modify the overall mobility of the polymer matrix chain**

CPA increased the Tg, Tc and Tf in PLA/OEO samples, so Oxygen reactive species could interact with OEO compounds, leading to decrease the plasticizing effect on PLA.

No effect of CPN treatment on the thermal properties of the films

*R. Salazar et al. / Polymer Degradation and Stability 97 (2012) 1871-1880
**Llana-Ruiz-Cabello et al. 2016. Food Additives and Contaminants - Part A, 33(8):1374–86.

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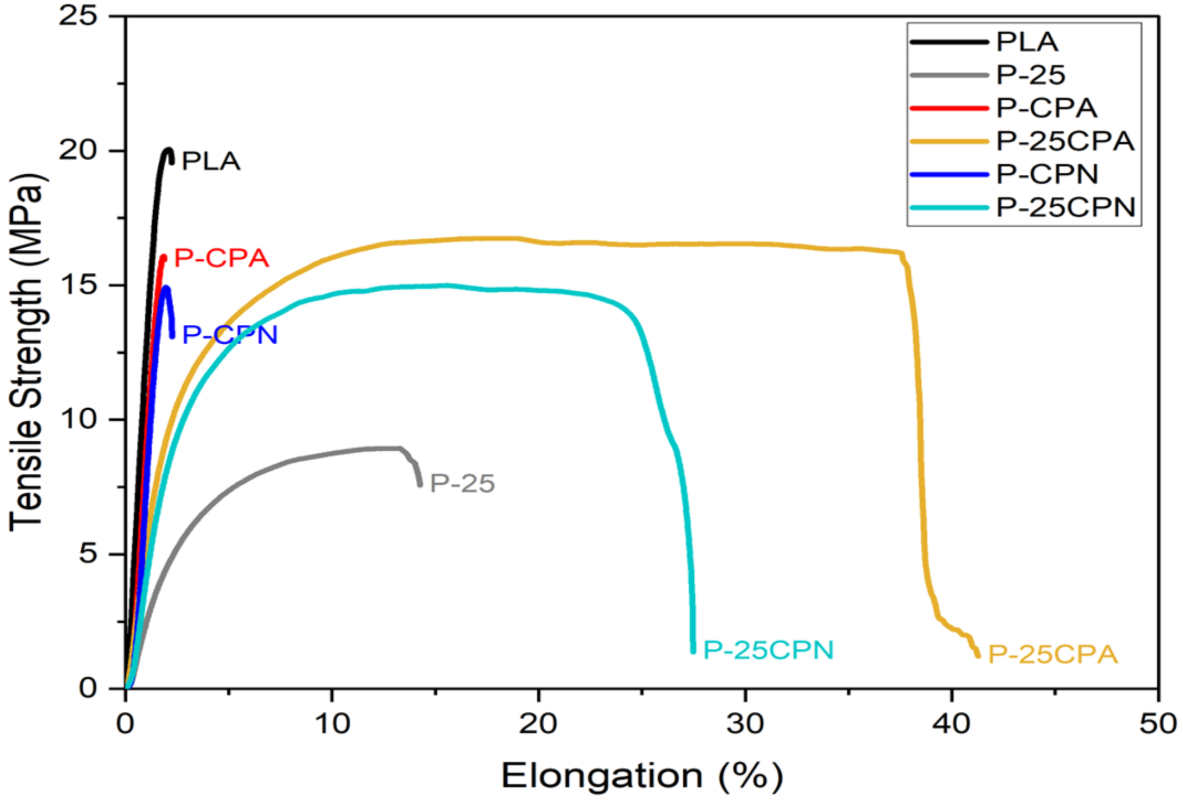
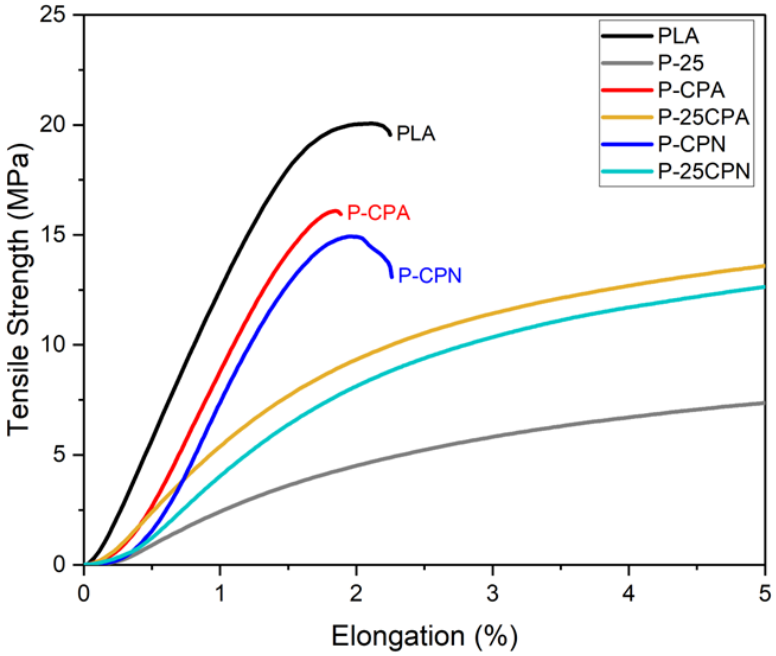
Results

Mechanical properties



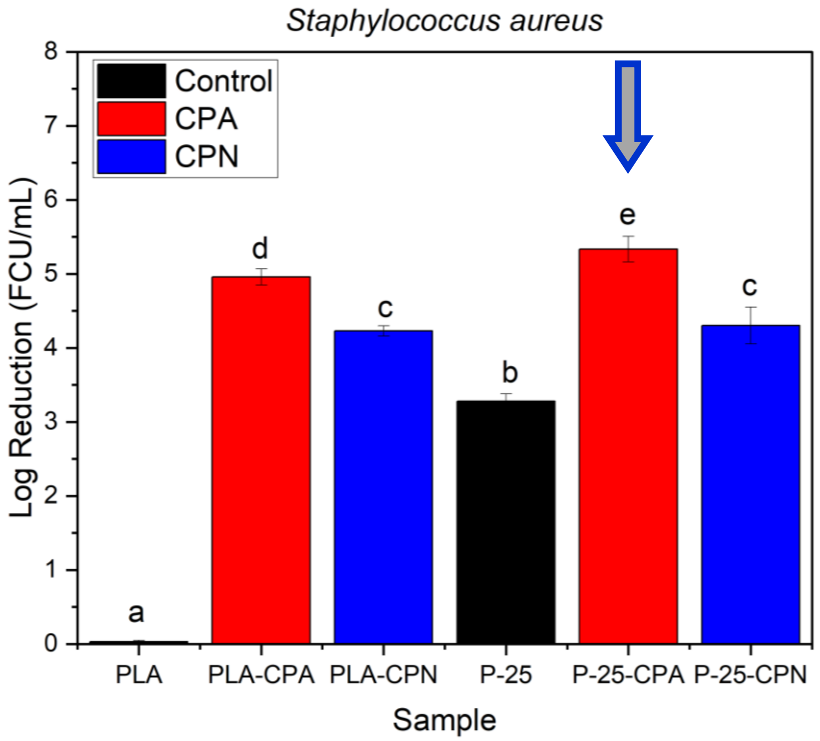


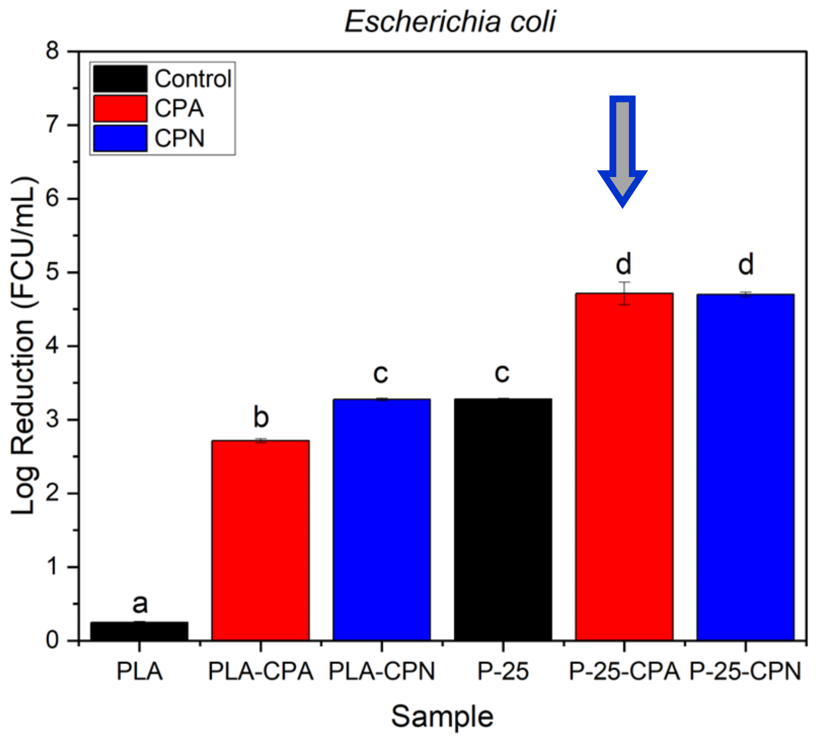
- PLA films with CP decreased the tensile strength

- Greater elongation with the incorporation of OEO.
- The tensile strength increased in the films PLA/OEO with CP treatment -> (35 °C > Tg of samples), treatment temperature effect?

Results

Antibacterial activity





CP produces reactive oxygen species (cytoplasmic membrane damage to proteins and DNA).

- PLA films treated with cold plasma air and nitrogen showed antibacterial activity.
- Greater reduction in P-25-CPA: 5.33 and 4.71 log UFC/mL for S. aures and E. coli, respectively.
- Sinergic effect of Cold plasma and OEO

Conclusions

- The properties of PLA films with 25 % oregano essential oil treated with cold plasma in an air and nitrogen atmosphere, were characterized regarding their thermal, mechanical and antimicrobial properties.
- OEO addition in PLA samples presented a plasticizing effect of films.
- CPA treatment decreased the plasticizing effect of OEO in the PLA films. CPN didn't affect the films.
- The addition of OEO increased the elongation at break of the samples.
- PLA film samples treated with cold plasma air and nitrogen showed antimicrobial activity.
- The samples of PLA with 25% OEO treated with cold plasma – air (P-25CPA) presented the greater bacterial reduction: 5.33 $\log_{10}$ CFU/mL against *S. aureus* and 4.71 $\log_{10}$ CFU/mL against *E. coli*.
- The results obtained are very promising for potential applications in the food active packaging industry.

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Thank you for your attention !

Contact : rvsalaza@espol.edu.ec