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Centro de Investigación en Alimentación y Desarrollo
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INFLUENCE OF NATURAL AND ARTIFICIAL WEATHERING ON BIOPLASTICS AND BIOCOMPOSITES FOR FOOD PACKAGING

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OUTLINE

Introduction

- **Solar irradiation**
- **Temperature**
- **Moisture**
- **Atmospheric oxygen (photooxidation)**

Experimental

- **Natural weathering**

Results

- **PLA+Glycerol+Chitosan+MA**

Summary

Acknowledgements

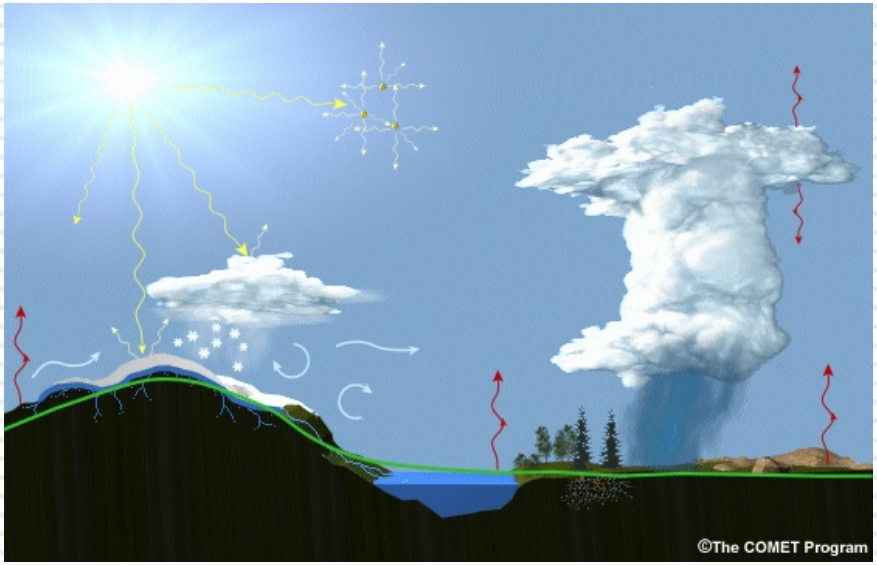
Q & A

INTRODUCTION

The aging of polymeric materials under natural and artificial conditions is a common test in plastic products.

Main environmental parameters evaluated in the degradation of polymers and plastics are:

- **Solar radiation**
- **Temperature**
- **Moisture**
- **Oxygen**



Solar radiation

Solar absorptivity is closely related to color, thus the color of samples will change by solar light exposure.

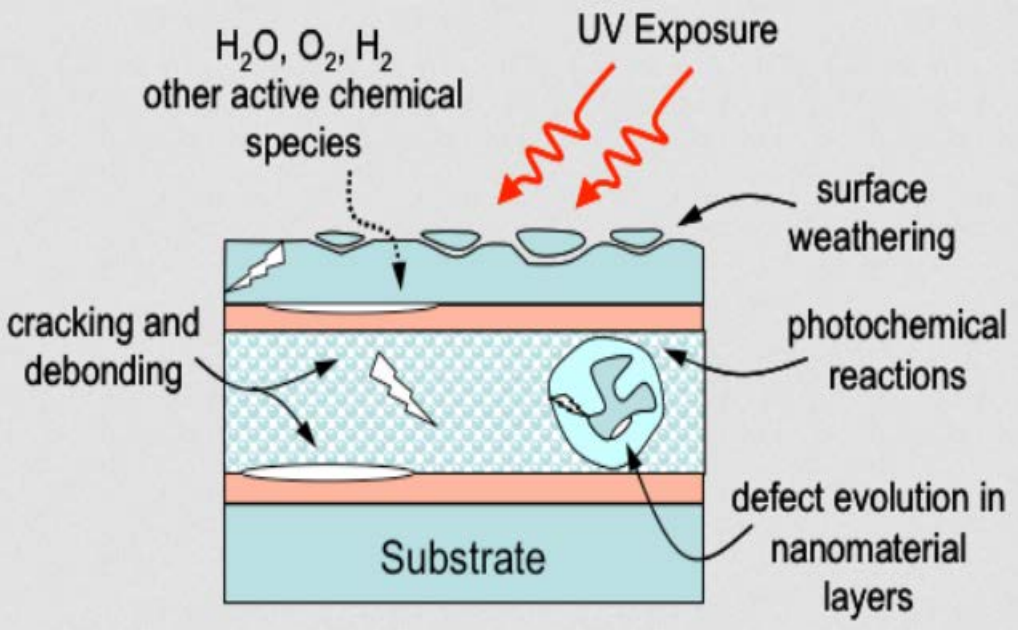
- **Short wavelength UV radiation causes yellowing.**
- **Long wavelength UV is primarily responsible for degradation of physical properties (tensile strength & impact strength).**





Because,

- **Short wavelengths are more strongly absorbed by most materials, have a greater effect on the layers close to the surface.**
- **Longer wavelengths penetrate more deeply into materials, where the physical property changes occurs.**



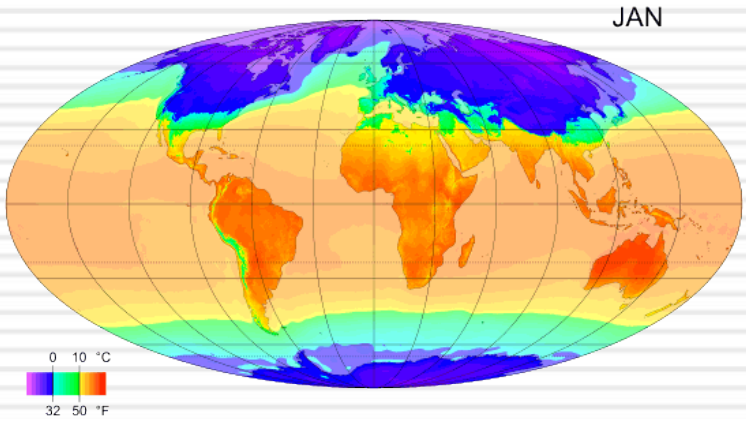
Mechanisms of degradation of polymer composites interfaces in outdoor environments.

S. Issacson. Stanford Univ. 2018

Temperature

Effects produced by temperature:

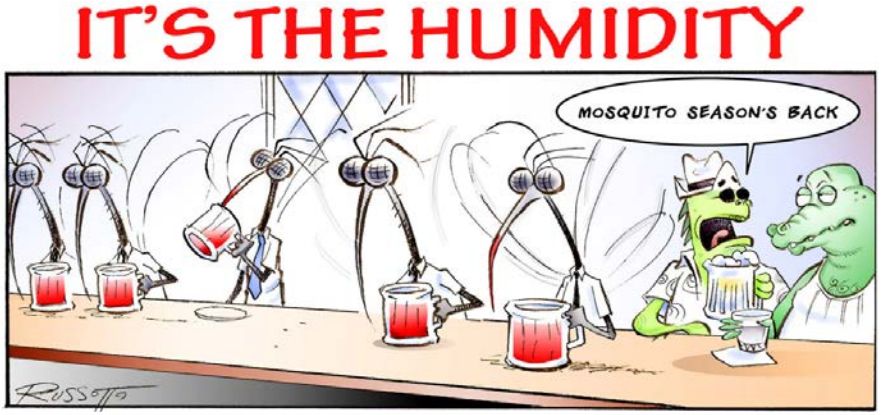
- **Molecules have greater mobility.**
- **Oxygen diffusion increases and formation of free radical from primary photochemical process.**
- **Water condensation on the material as dew, a rise in temperature causes evaporation, and a rainfall can cause thermal stress.**



WorldlyWise.com

Moisture

- Moisture and solar radiation, contributes significantly to the weathering of polymeric materials.
- Mechanical stresses imposed when moisture is absorbed or desorbed. Chemical participation of moisture cause weathering.
- Water absorption - surface layers - volume expansion - mechanical stress on dry subsurface layers.
- Drying out of the surface layers would lead a volume contraction.



Atmospheric oxygen

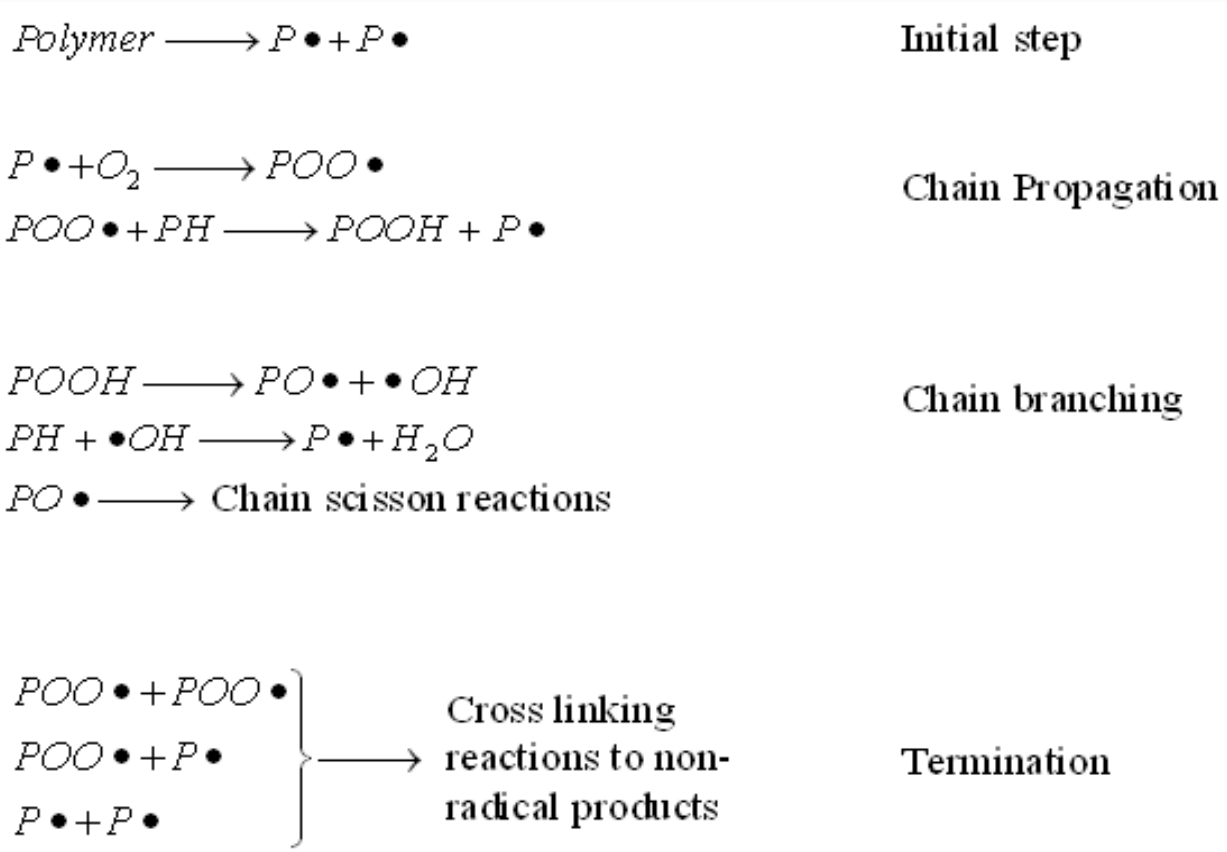
Photooxidation: solar radiation combines with oxygen.

Free radicals: the cleavage of chemical bonds by solar radiation, react with O_2 to form peroxy radicals that initiate a series of radical chain reactions.

Photochemical reactions involving O_2 - inner and outer layers of aromatic or aliphatic polymers - dependence on the diffusion of O_2 through the polymer.



UV damaged polypropylene rope (left) and new rope (right)



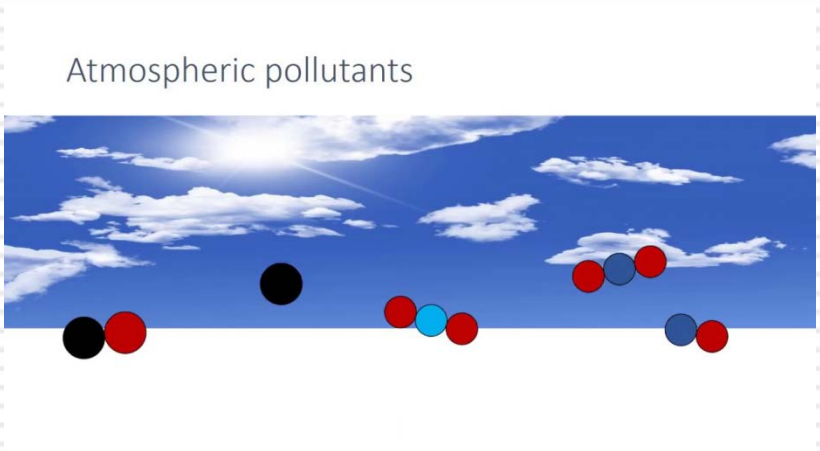
Where:

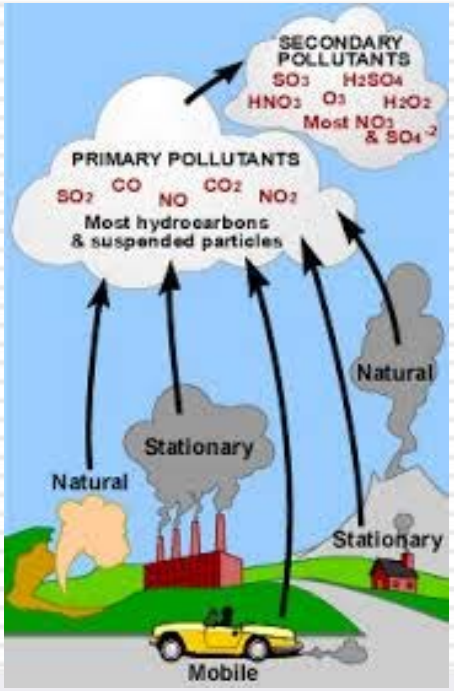
PH = Polymer P• = Polymer alkyl radical PO• = Polymer oxy radical (Polymer alkoxy radical) POO• = Polymer peroxy radical (Polymer alkylperoxy radical) POOH = Polymer hydroperoxide HO• = hydroxy radical

Rabek & Ranby, J Polym Sci. Polym Chem. 12(2):273-294, 1974.
Yousif & Haddad, SpringerPlus. 2:398, 2013.

Secondary factors of Weathering

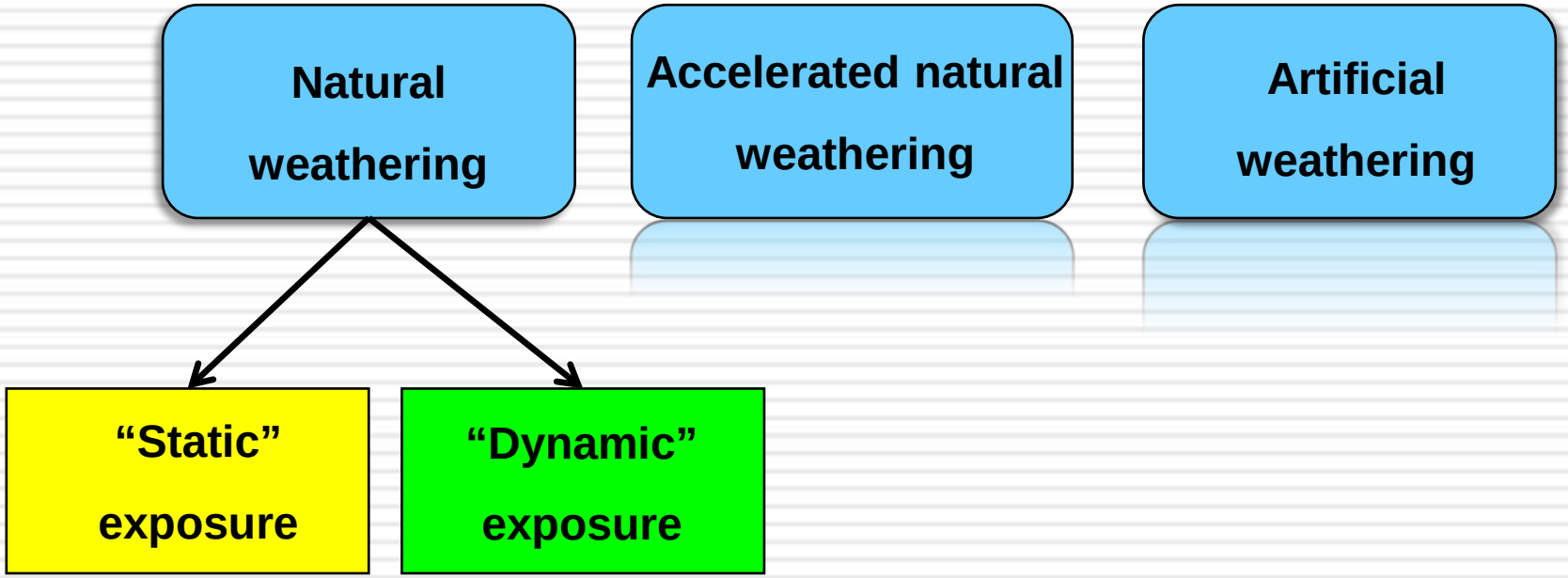
- Ozonolysis, typically produces a stiffening and cracking, particularly under mechanical stress.
- Atmospheric pollutants (Sulfur dioxide + solar radiation + O_2) = X-lking of PE & PP, loss of color in pigmented coatings.
- Moisture + temperature = microbial growth, may cause material degradation.





Weathering testing of polymers

To determine the polymer degradation and polymer coating degradation under lab or natural condition.



Accelerated weathering



QUV accelerated weathering tester

NOM: ASTM G154

Exposition time: 0, 100, 200, 300, 400 y 500 h.



Q-Sun Xenon arc test chamber

NOM: ASTM G155

Exposition time: 0, 100, 200, 300, 400 y 500 h.

EXPERIMENTAL



Natural weathering

Exposition place: Hermosillo, Sonora Mexico.

Climate: Primarily arid or semiarid deserts and grasslands, the highest elevations having sufficient rainfall to support other types of vegetation.

Time of exposition: September to February or March to August

Location: 29.10° Lat. and -110.98° Long. and at Elev. 212 m above sea level.



Materials

PLA-Chitosan biocomposite:

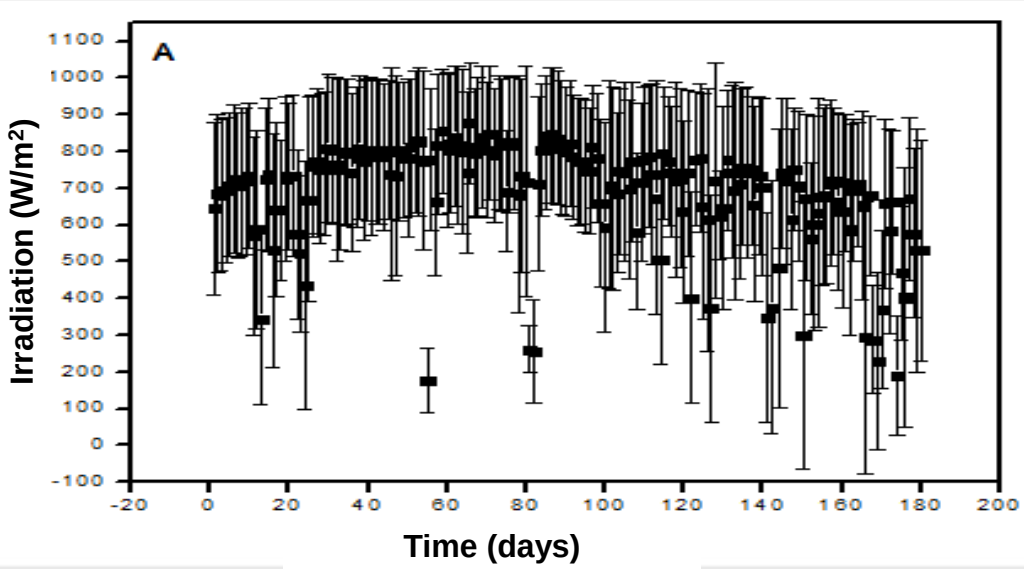
Polylactic acid (Ingeo 4043D) NatureWorks.

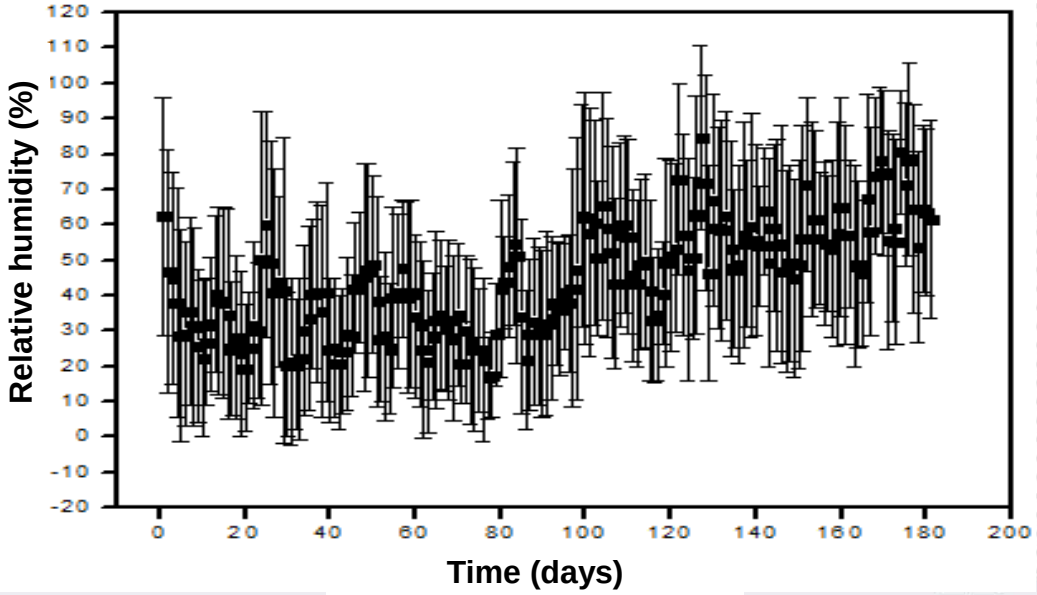
Glycerol, Chitosan (0, 3, and 5% wt), Maleic anhydride (MA) and

Dycumil peroxide (DCP) from Sigma-Aldrich.

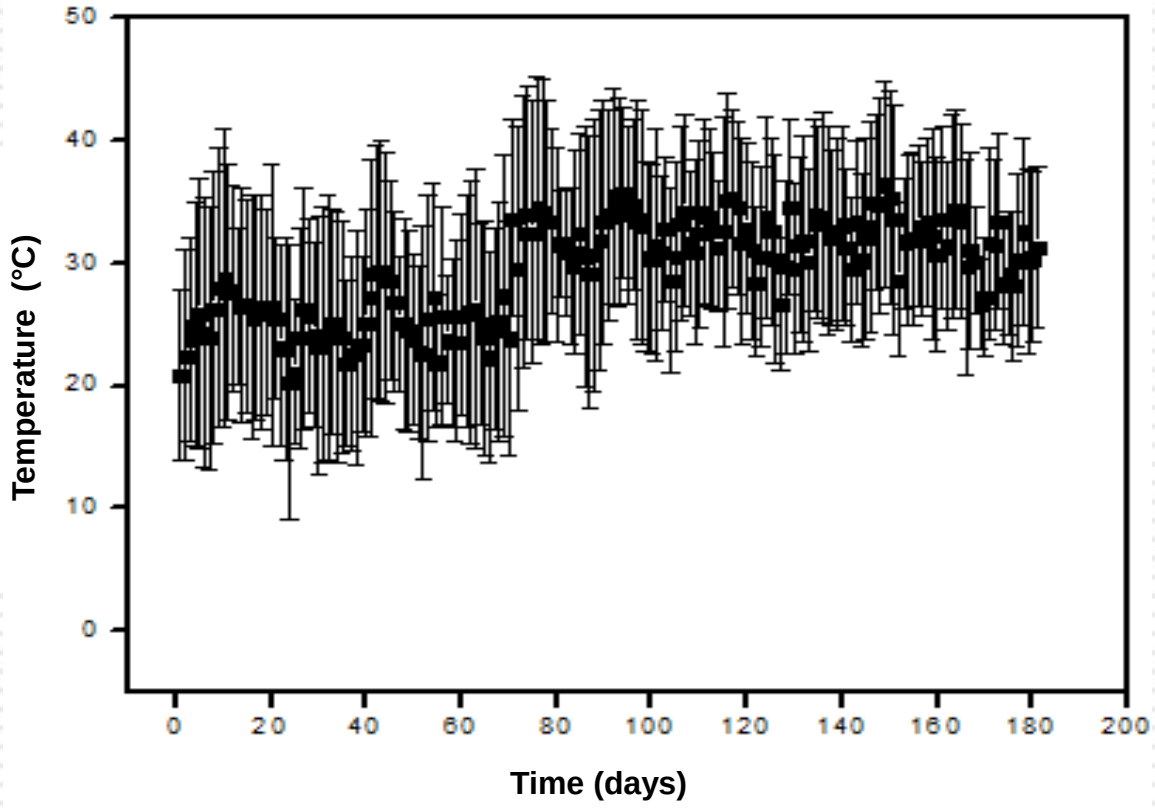
(Natural weathering)

Environmental conditions





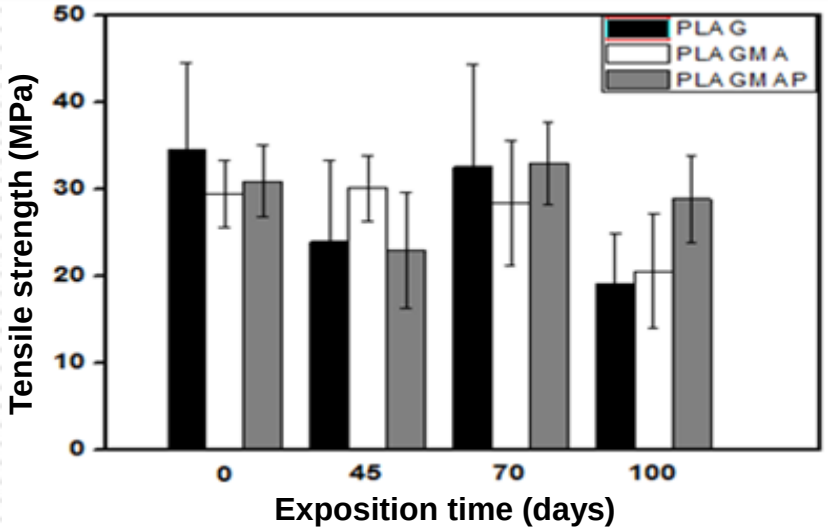
Environmental conditions

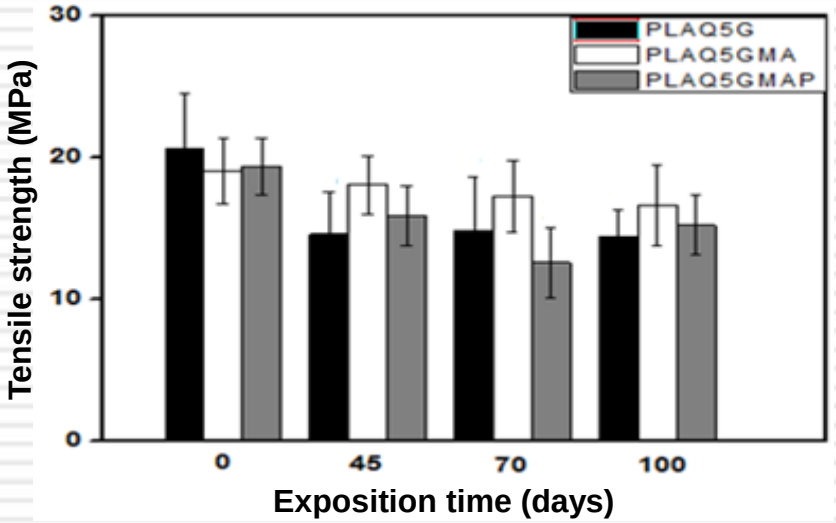


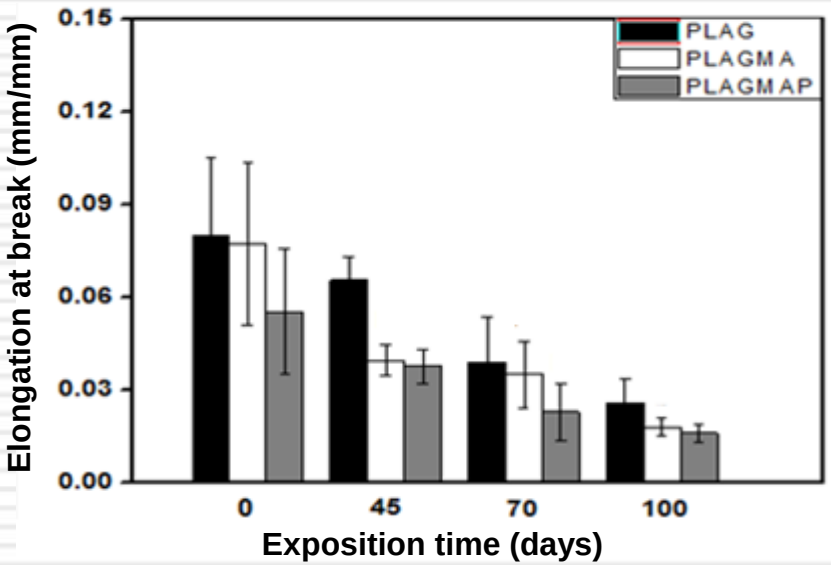
RESULTS

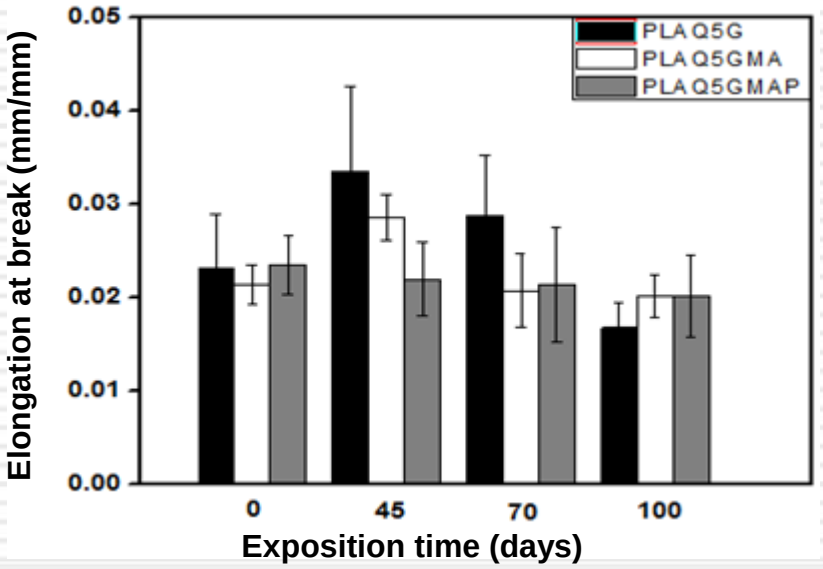
Mechanical properties

5% Chitosan



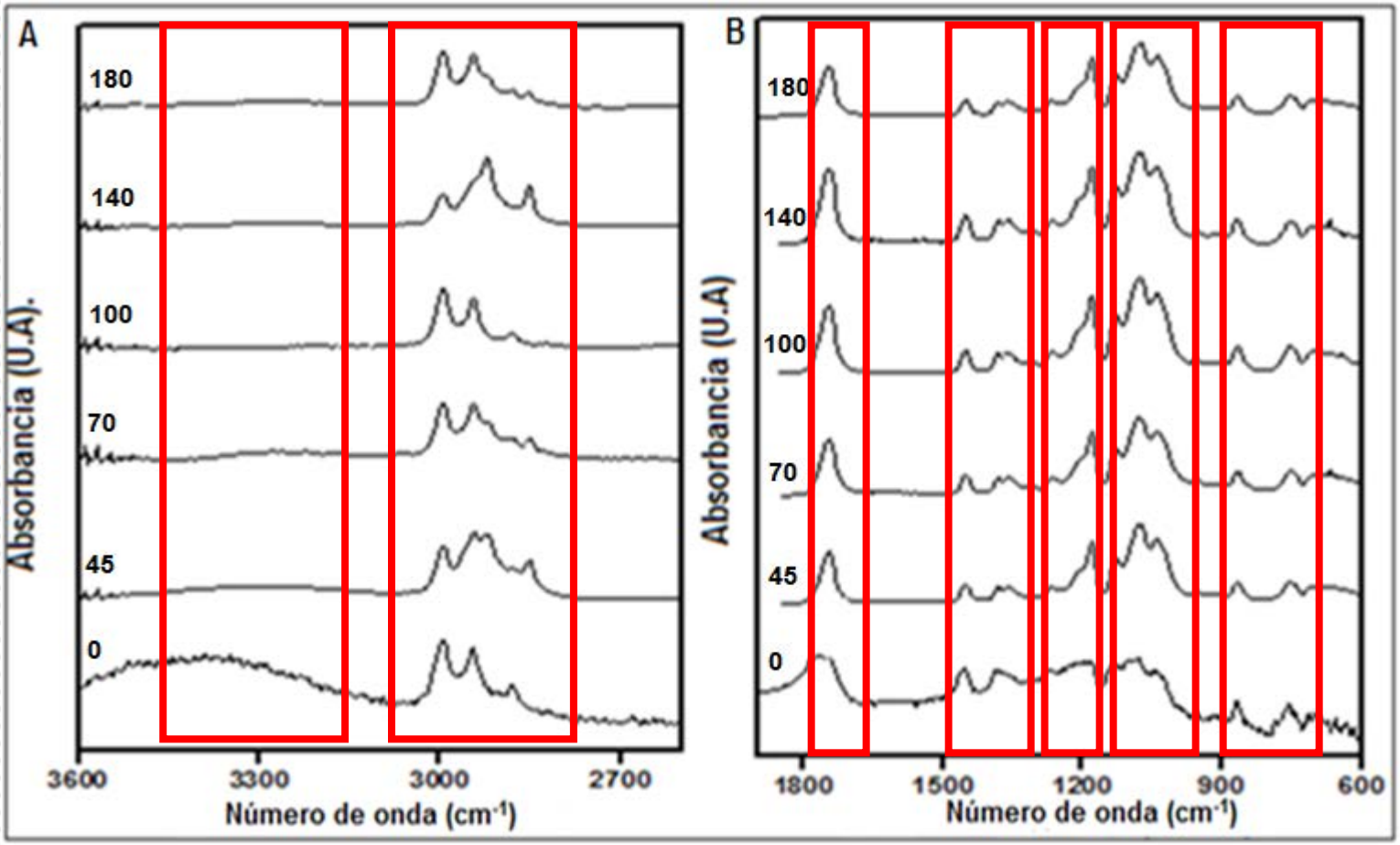






FTIR

Formulation: PLAGMAP



Numbers indicate exposition time in days.

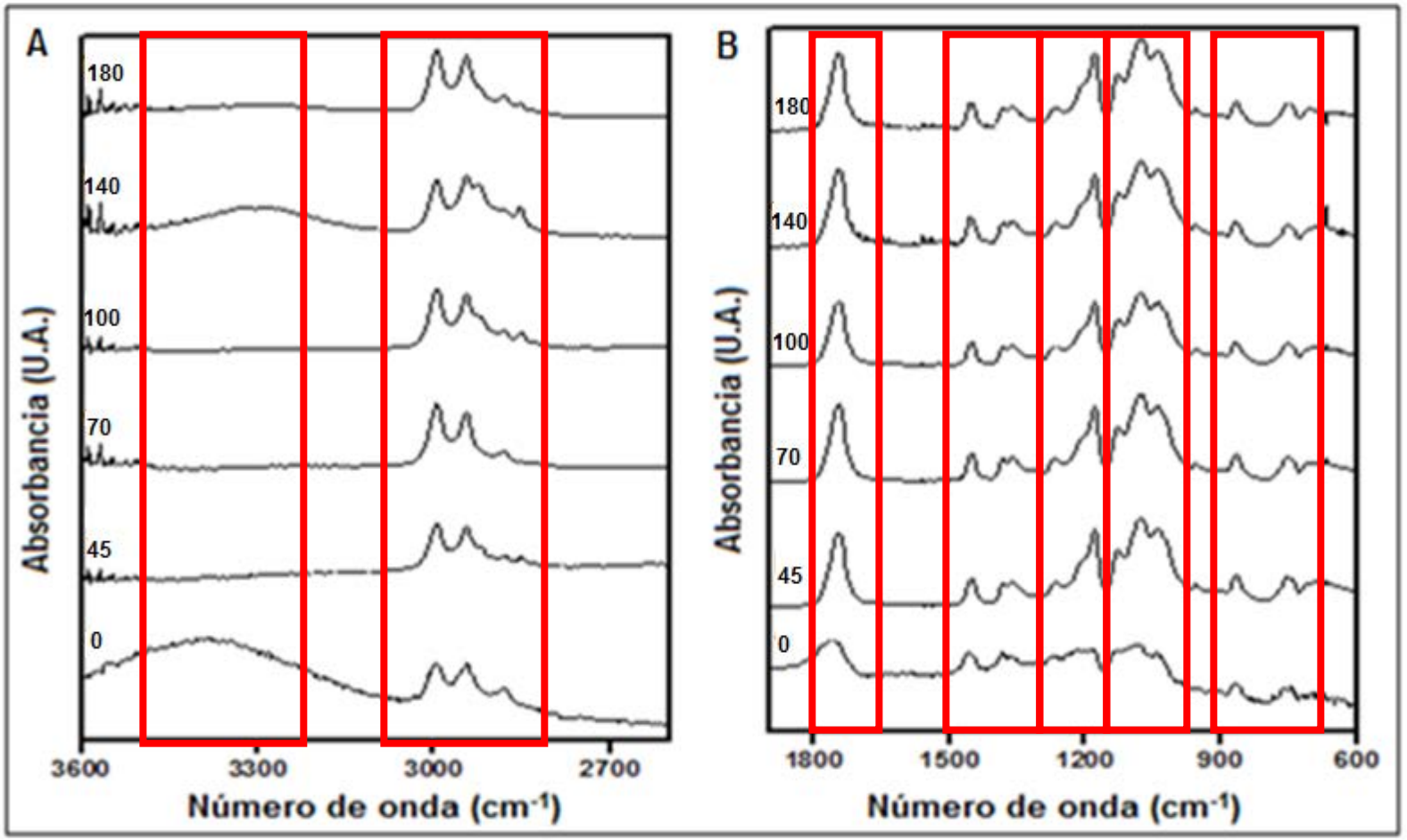
OH CH_2, CH_3 (Stretching) **C=O CH_2, CH_3 (Flexion) C=O, C-O-C**

C-O bonds related to OH **Amorphous and semicrystalline regions PLA**

Zou y col, 2009; Rodríguez y col, 2014; Spiridon y col, 2013

FTIR

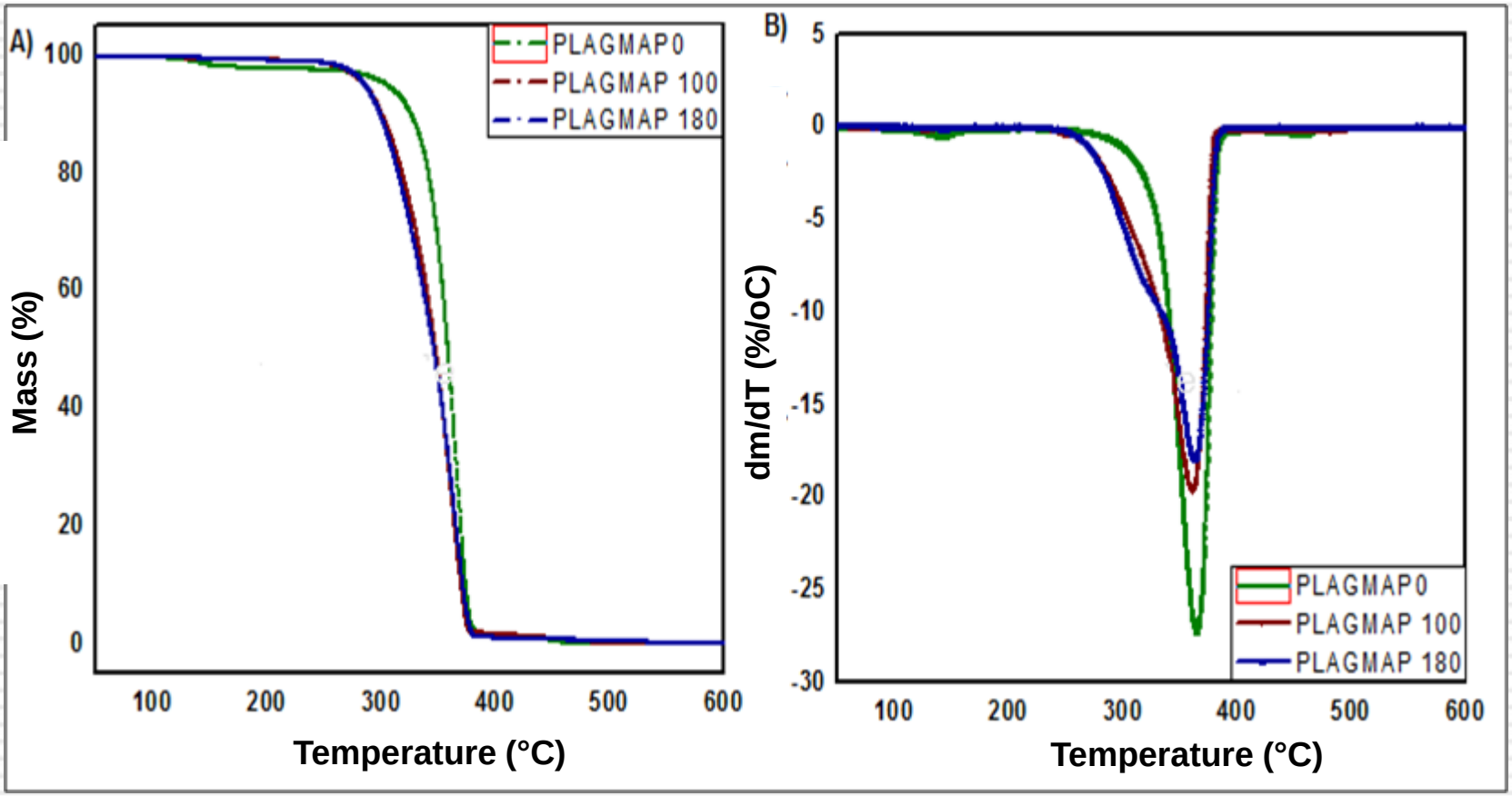
Formulation: PLAQ5GMAP 5% Chitosan



OH,NH CH_2, CH_3 (Stretching) C=O CH_2, CH_3 (Flexion) C=O, C-O-C

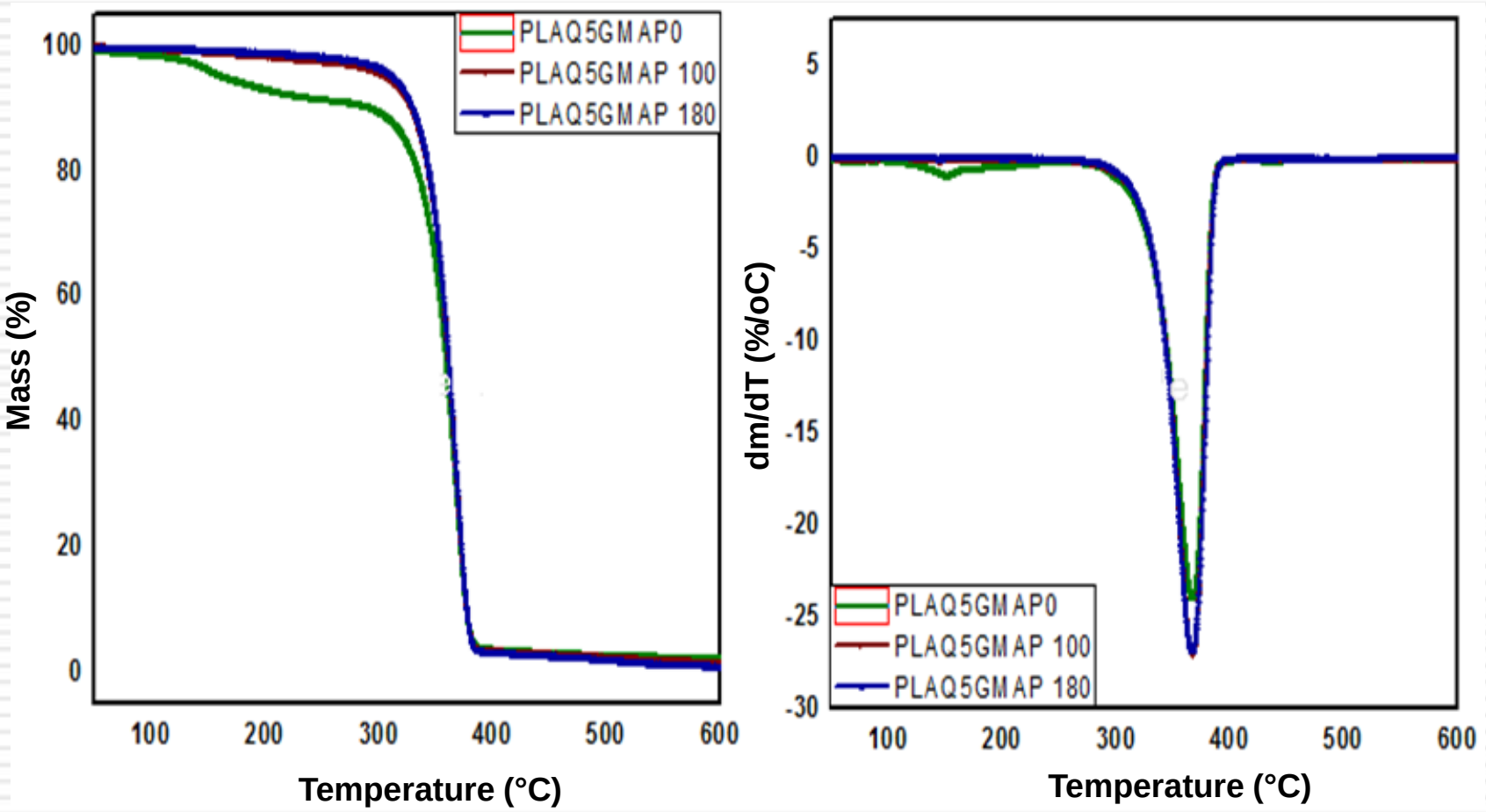
C-O , C-N related to OH and NH Crystalline and amorphous regions of PLA

Thermogravimetric analysis



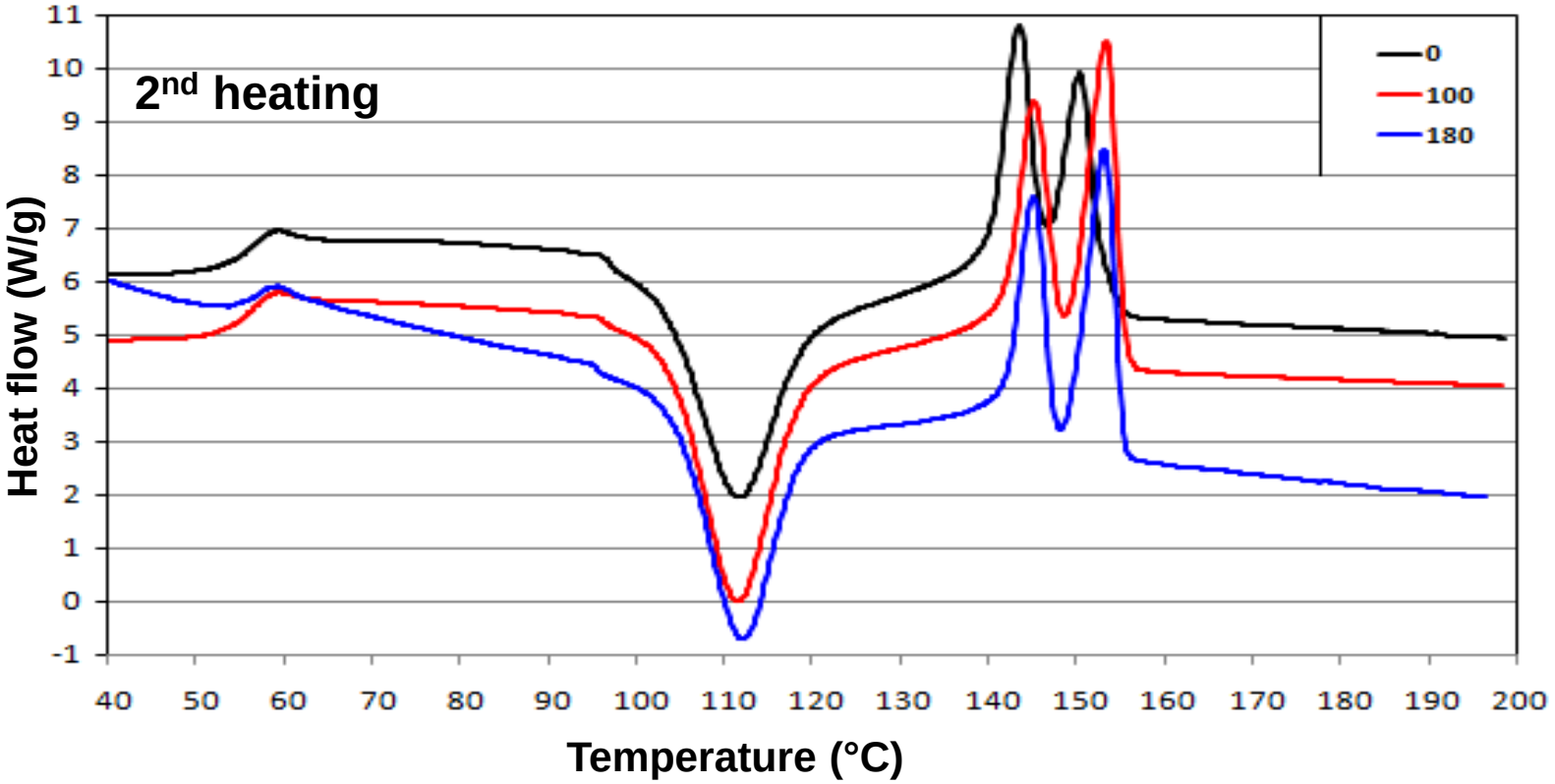
Thermogravimetric analysis

5% Chitosan



DSC

Formulation: **PLAGMAP**

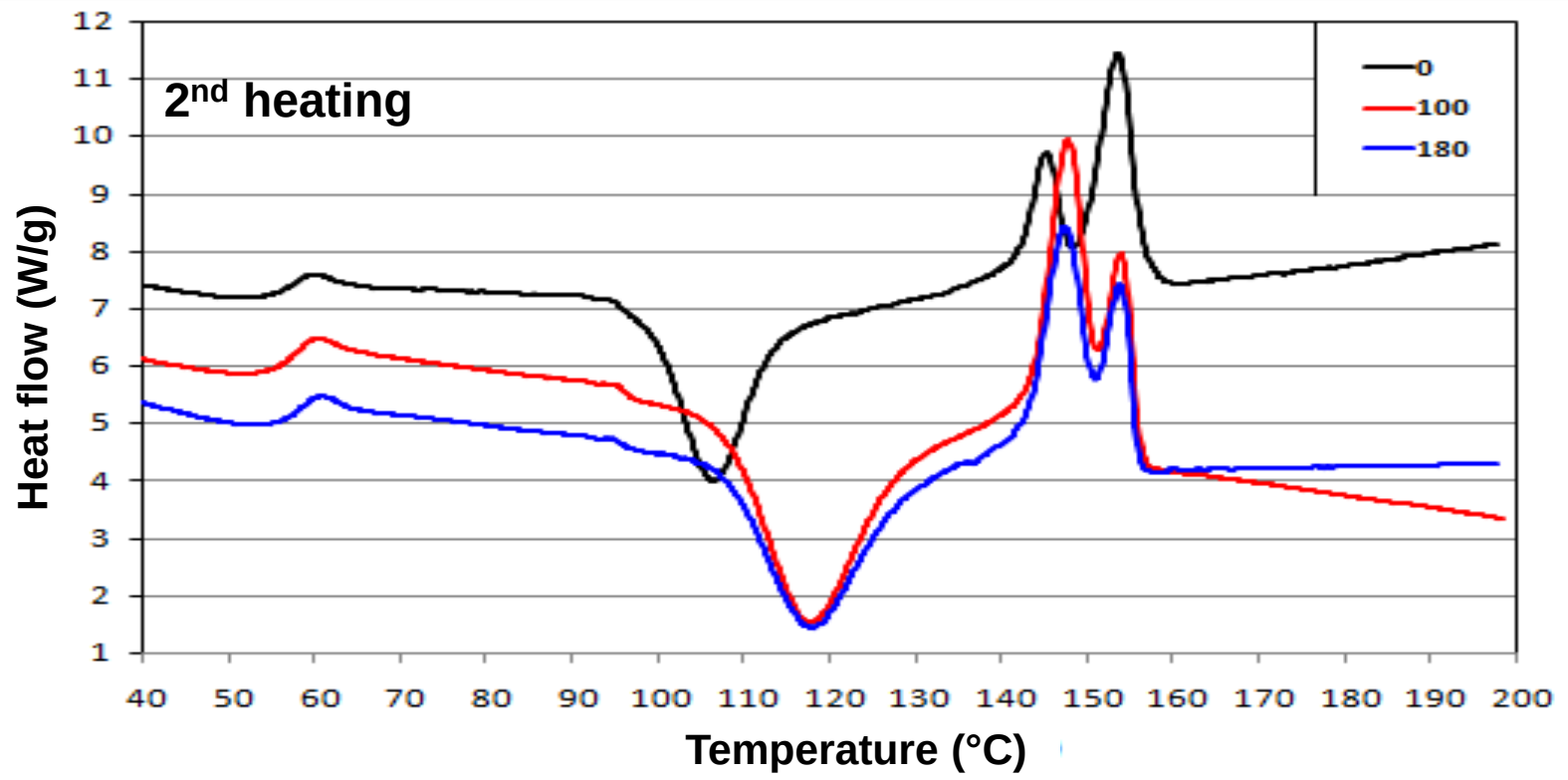


Tg = 55.18 - 55.48 °C, Tc = 111.5 – 111.93 °C,

Tm^1 = 143.3 - 145.03 °C, Tm^2= 150.4 - 153.3 °C

DSC

Formulation: **PLAQ5GMAP**



Tg = 56.8 - 57.5 °C, Tc = 103.5 – 117.9 °C,

Tm^1 = 145.1 - 147.6 °C, Tm^2= 153.5 - 153.9 °C

Optical microscopy

Surface morphology of biocomposites:

A) PLAGMAP,

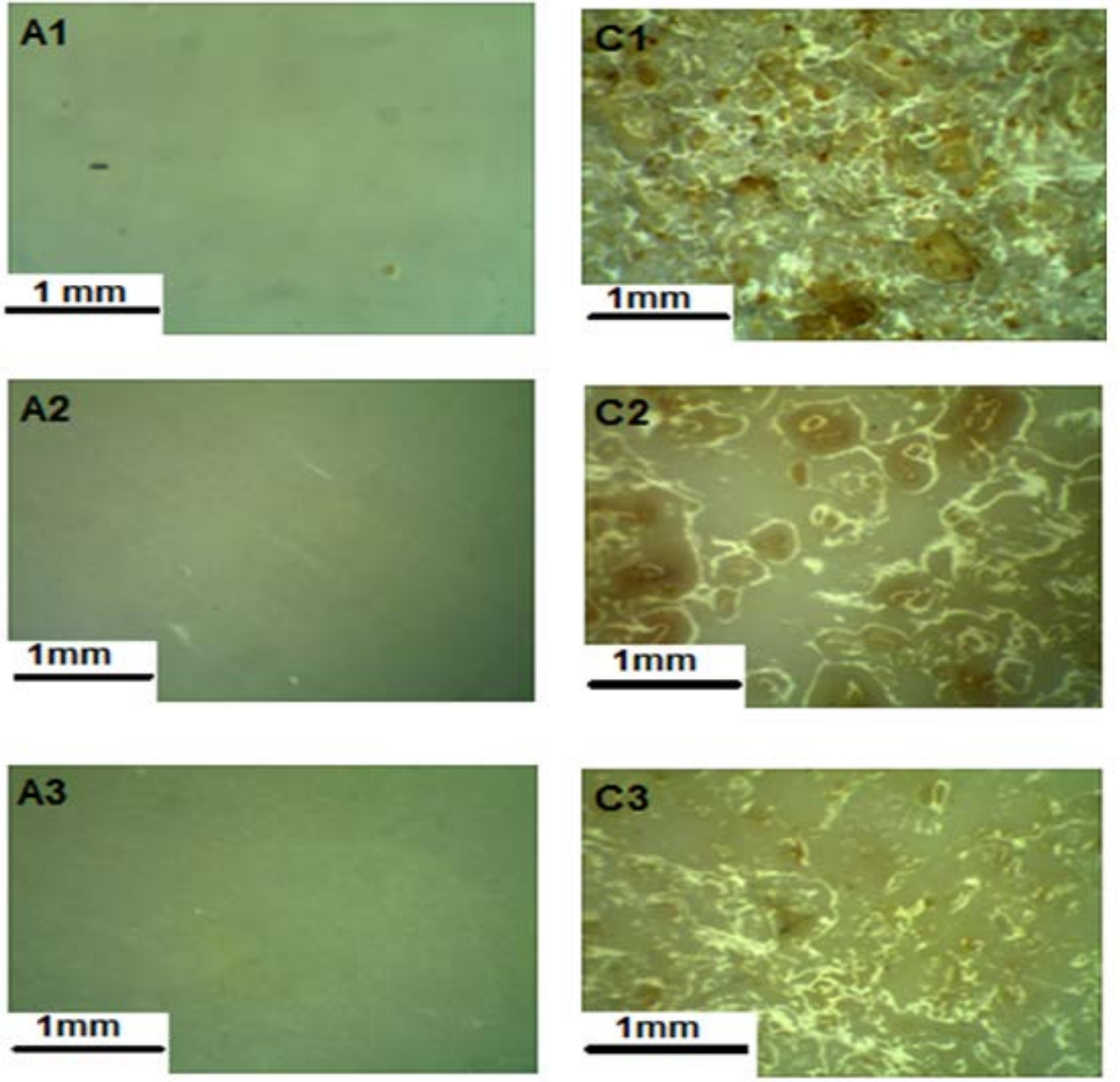
C) PLAQ5GMAP

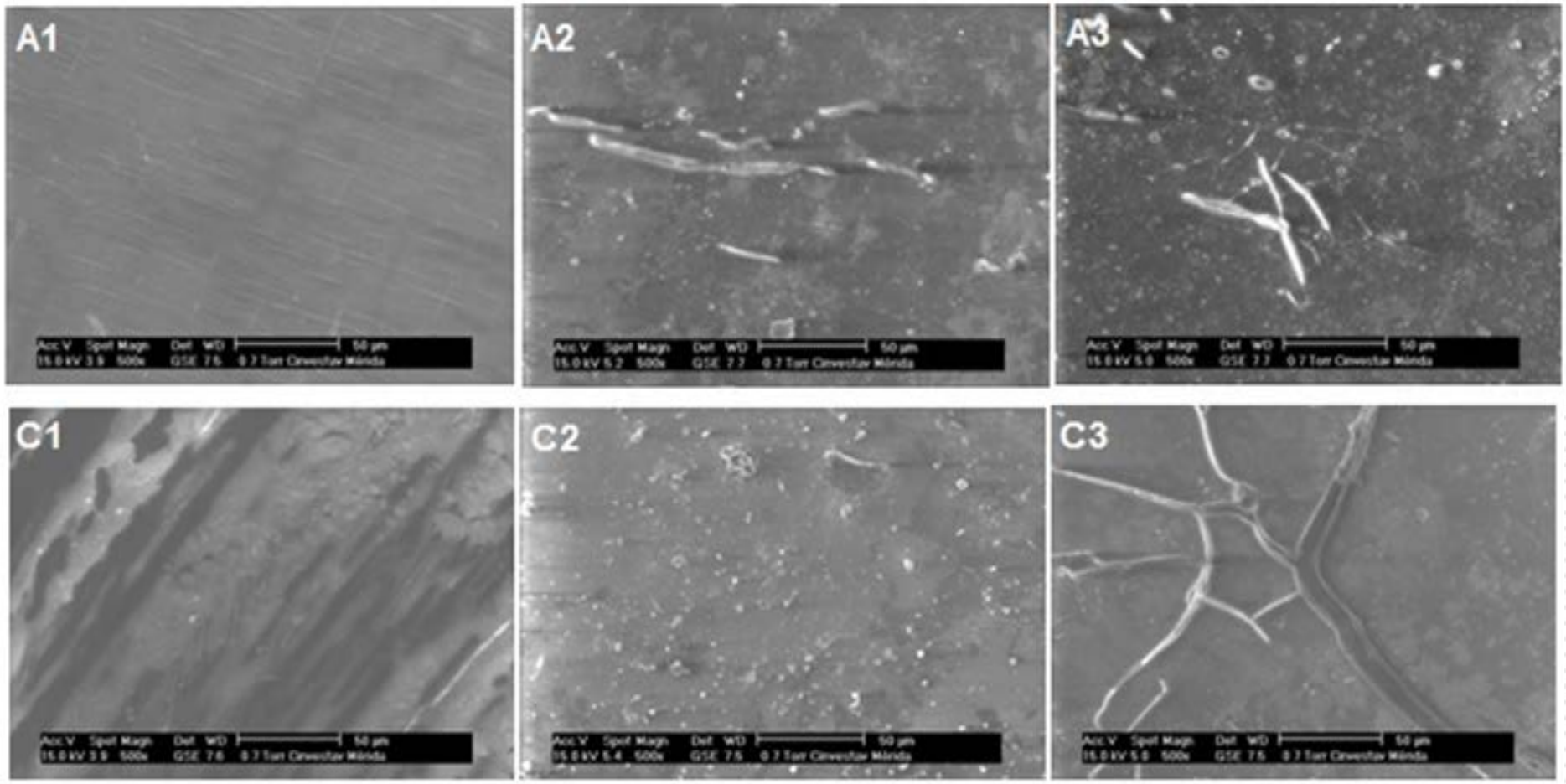
At different exposition days:

1) 0 days,

2) 100 days, and

3) 180 days.





Biocomposites: (A) PLAGMAP and (C) PLAQ5GMAP.
Exposition time: (1) 0, (2) 100, and (3) 180 days. At 500X magnification.

Summary

Photodegradation of PLA-Chitosan biocomposites were evaluated by natural weathering for 180 days between March to August 2016.

A reduction of mechanical properties (TS), modification of structural properties and intensification in the samples color were observed. The surface morphology showed microfractures on the samples.

The descomposition temperatures did not show significant changes, although melting temperature (and enthalphy) showed an increase when chitosan was added.

Even though, PLA+Chitosan biocomposites showed the degradation of exposition to natural weathering, the results show dependency with a component factor (weather).

Acknowledgments

Red Temática de Intemperismo de Materiales Plásticos. CONACyT



Thank you very much for your kind attention

Questions?

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