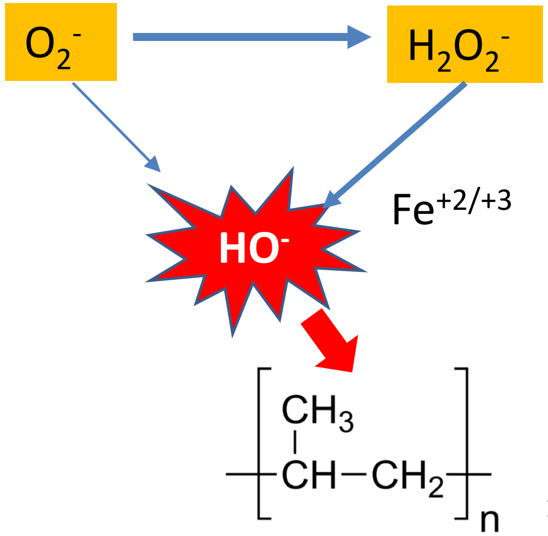
# Accelerating Polymer Degradation using Pro-oxidant Additives


**Endalkachew Sahle-Demessie, and Bineyam Mezgebe**

US EPA/ Office of Research and Development

Center for Environmental Solution and Emergency Response

Cincinnati, OH 45040

# Why is plastic a problem?

EPA

- Plastic is considered to have made the modern world possible. (used for surgical gloves, food storage, water pipes, wires and cable coating, cell phones, packaging, telephones, TVS))

The problem:

(1) 45% of plastics goes to single-use items (disposables, packaging, table ware...).
e.g., the U.S. use 100 billion plastic bags per year.

(2) plastics do not degrade, they not easy for recycling or reuse. A large volume end up in landfills or pollute the environment.

(3) Plastic bags take 400 – 1,000 years to biodegrade→ Persistent


*"There is no such thing as AWAY because plastic is so permanent and so indestructible that when you cast it into the ocean it does not go AWAY."*
*Sir David Attenborough*

**Alternatives**: substitute such as paper, biopolymers – expensive or other life cycle impacts

Source: https://www.globalcitizen.org/en/content/bbc-plastic-2020-blue-planet-sir-david-attenboroug/

**Sustainable Solution**

**Add prooxidant to make a low-cost plastic that has a good service performance, but environmentally degradable**

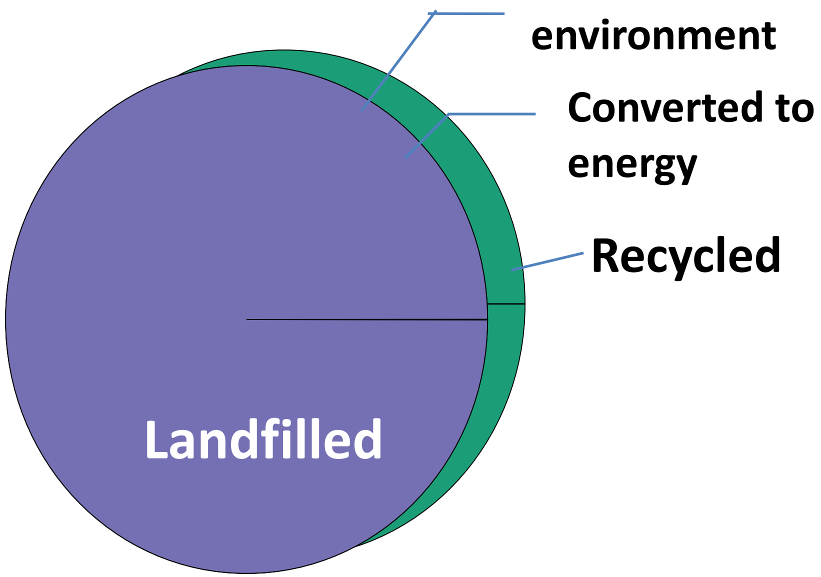
# Plastics Pollution a Global Challenge

**Essential:** Plastics are considered to have made the modern world possible. (used for packaging, construction materials, automotive, electrical devices)

**The problem**:

- 45% of plastics goes to single-use items (disposables, packaging, table-war, plastic bags)
- Improper management of plastic waste led to macro - & micro plastic pollution
- Plastics do not degrade, not easy for recycling or reuse. Plastic ***persist*** and pollute the environment.

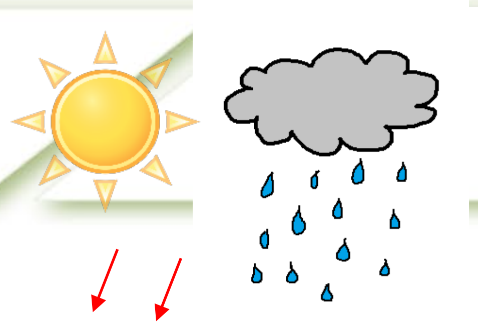
**End-of-life of plastics**

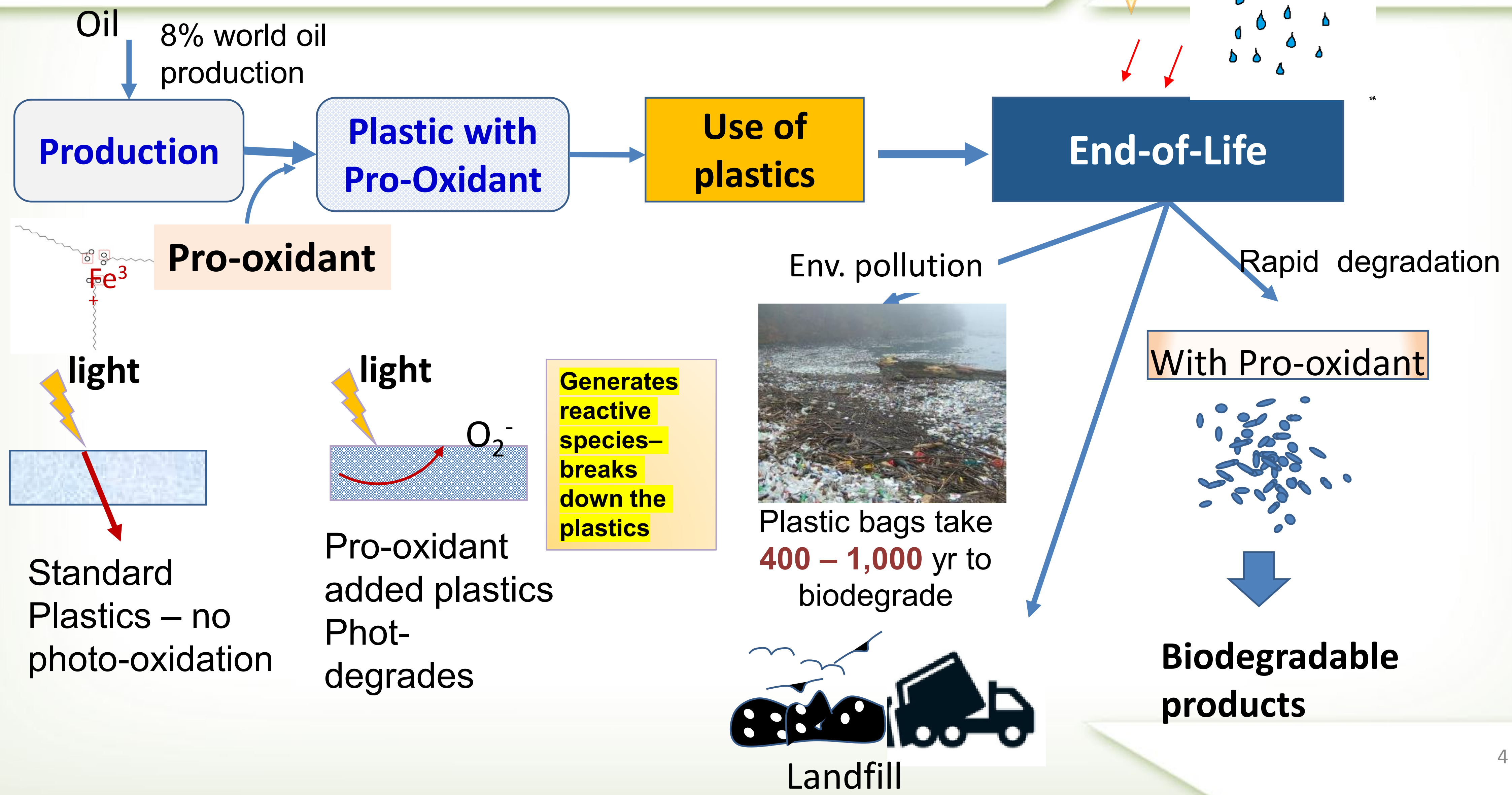



**Alternatives**: substitute paper, biopolymers – expensive or higher life cycle impacts

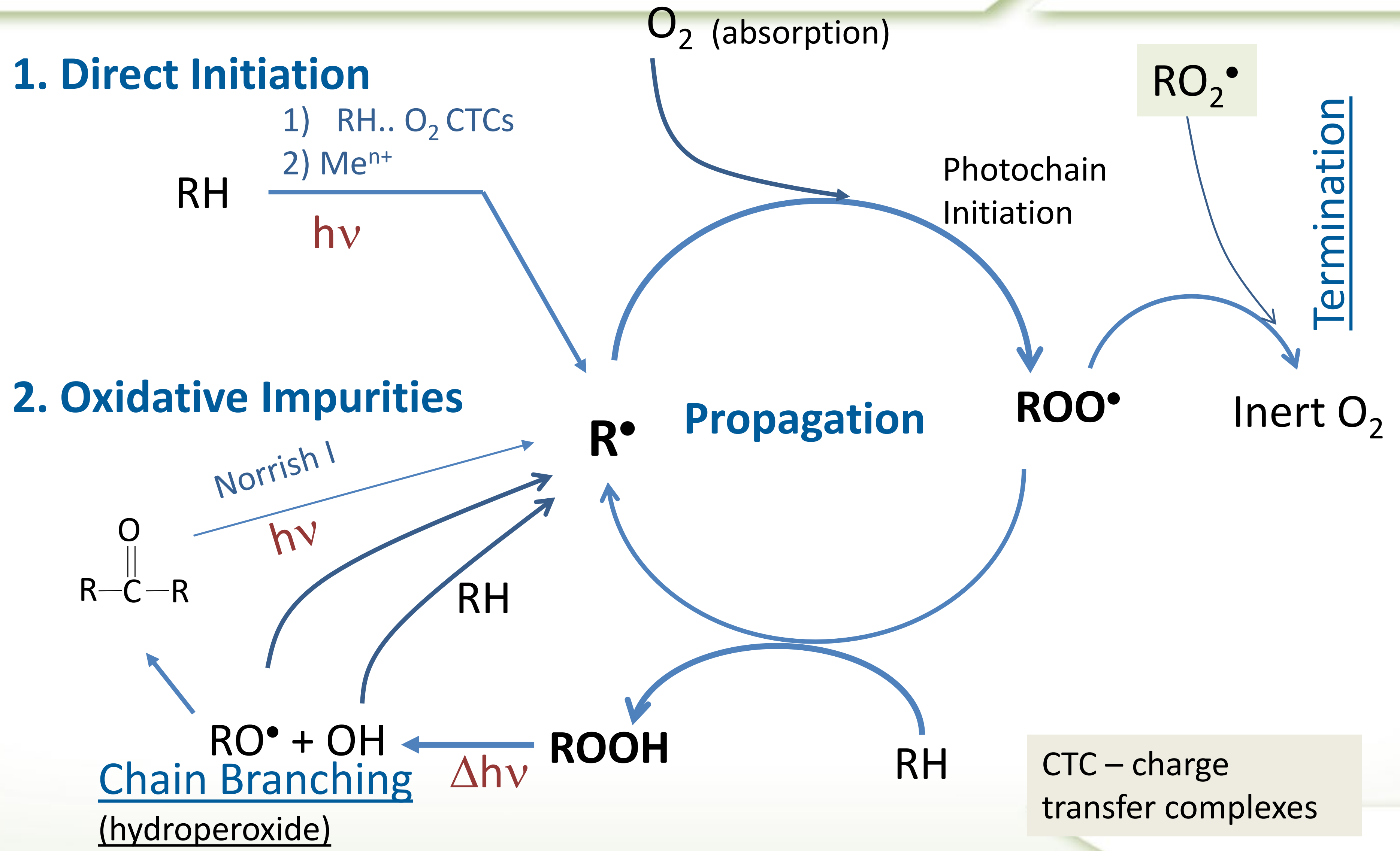
**Eliminate persistence of plastics by adding a safe pro-oxidant to make a low-cost biodegradable plastic**

# Life cycle stages of plastics





# Photooxidation of polymers: Chain and Photochain Mechanism



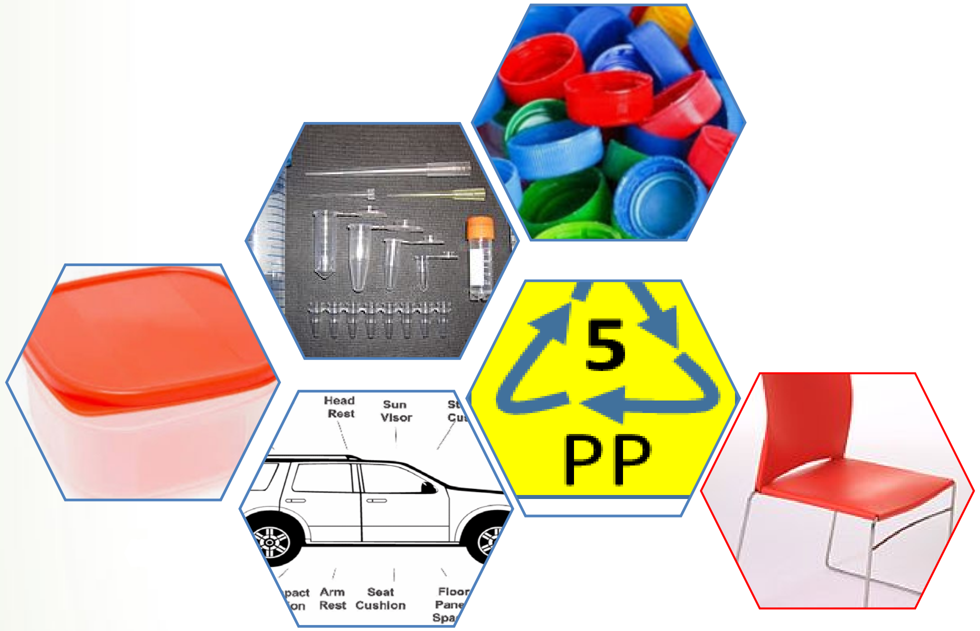
# Research Objectives

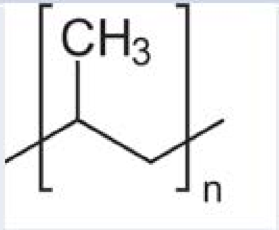
**Hypothesis**: Adding *pro-oxidants* significantly accelerates photo-degradation of plastics and become biodegradable

- What are the effects of pro-oxidant additives on plastics?
- How fast do pro-oxidant increase the rate plastic degradation?
- Does the type and amount of pro-oxidant affect the rate of plastics degradation?
- Do pro-oxidants affect physical and chemical properties of the plastics?
- What are degradation by-products, and are they biodegradable

# Properties of Polypropylene

Polypropylene is *Thermoplastic* – stable semi-crystalline plastic




| | Properties |
|---|---|
| **General properties** | High flexible strength, resistant to moisture, resistant to organic solvents and acids |
| **Chemical Structure** $(C_3H_6)_n$ |  |
| **Melting Point** | Approx. 160 ° C |
| **Applications** | Automotive parts, packaging, toys, lab equipment, furniture. |

# Test materials for plastic aging

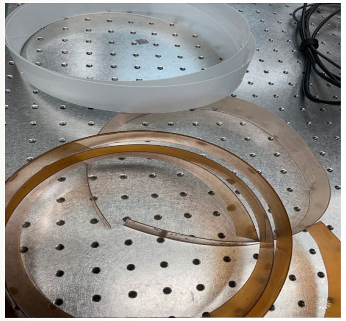
| Polymer | Dimension | Pro-Oxidant | Pro-oxidant amount (% w/w) | Pro-oxidant amount (% w/w) |
|---|---|---|---|---|
| Polypropylene | 0.1x5x100 cm | (no filler –control) | 0 | 0 |
| Polypropylene | 0.1x5x100 cm | Ferric stearate $C_{54}H_{105}FeO_6$ | 1 | 2 |
| Polypropylene | 0.1x5x100 cm | Cobalt stearate $C_{36}H_{70}FeO_4$ | 1 | 2 |

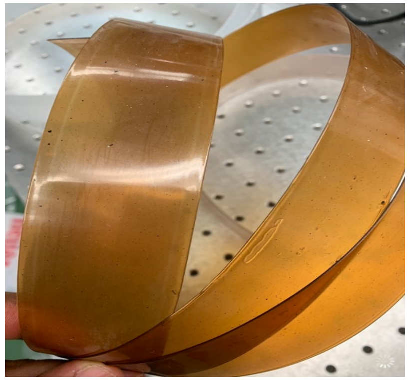
# Making Polypropylene (PP) films with Prooxidant

PP beads

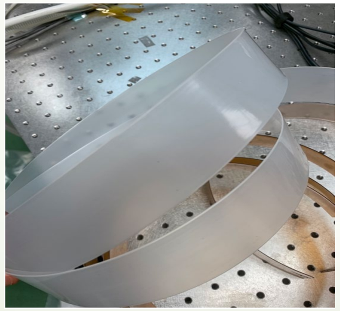
Melt PP Mix with Pro-oxidants

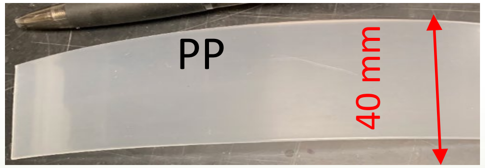
**Screw extrusion**





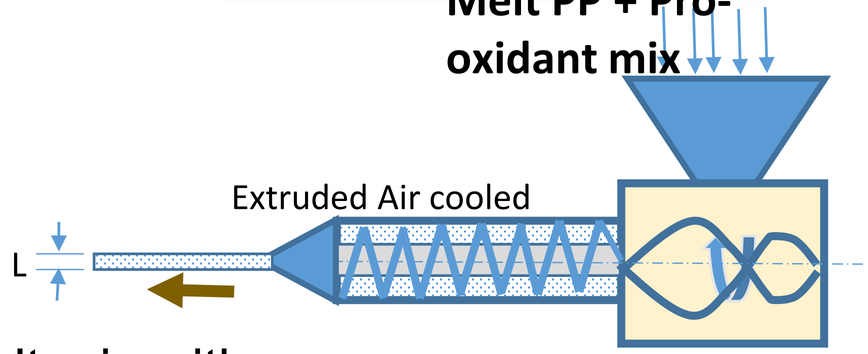
PP+2%Fe-stearate






Thickness 1 mm

**Melt PP + Pro-oxidant mix**

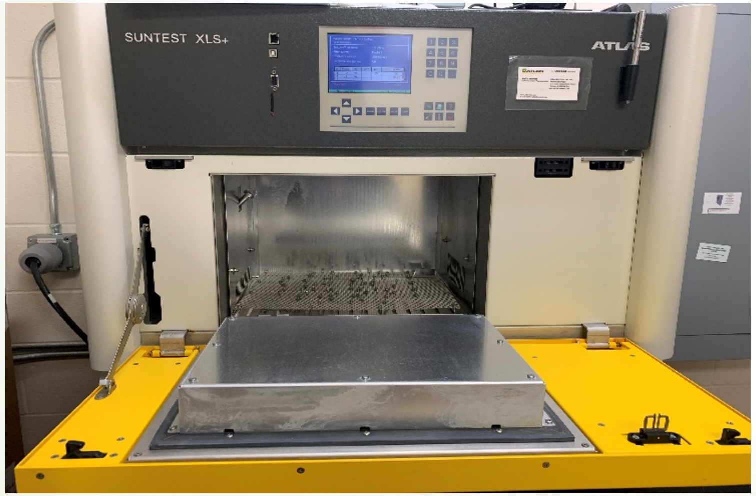



T > 150 $^{o}$C

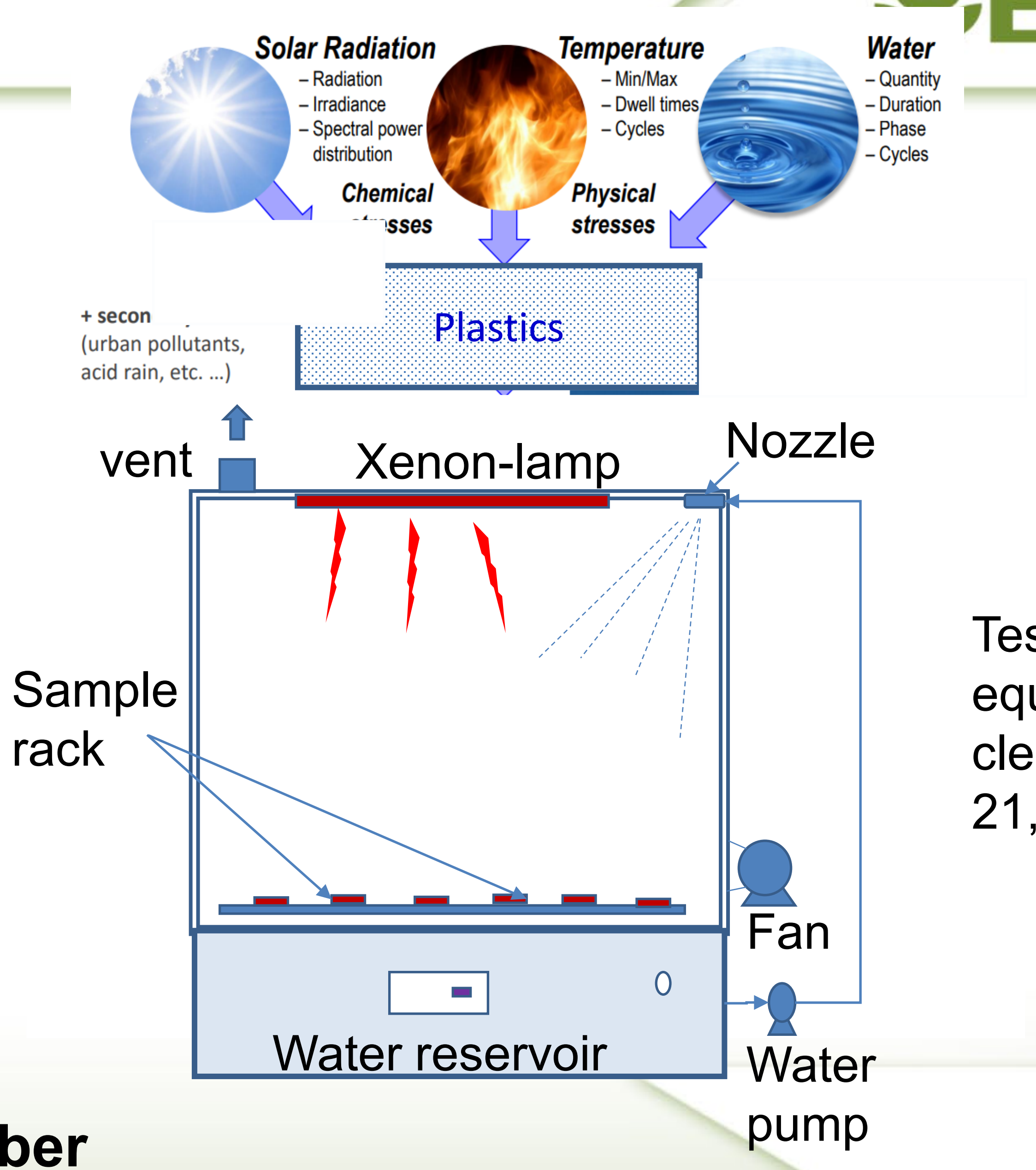
Melt mix with screw extruder

# Accelerated aging – Combine effects of UV light -heat-rain

| Parameter | Condition |
|---|---|
| A cycle of weathering | 120 min (sunshine: 108 min, rain: 12 min) |
| Humidity | 8-20% for sunshine and over 60% for rain |
| Solar light irradiation | 700 W/m$^2$ |
| Wavelength of solar light | 300-800 nm |
| Chamber temperature | 33-37 $^oC$ |
| Black substance temperature | 65 $^oC$ |

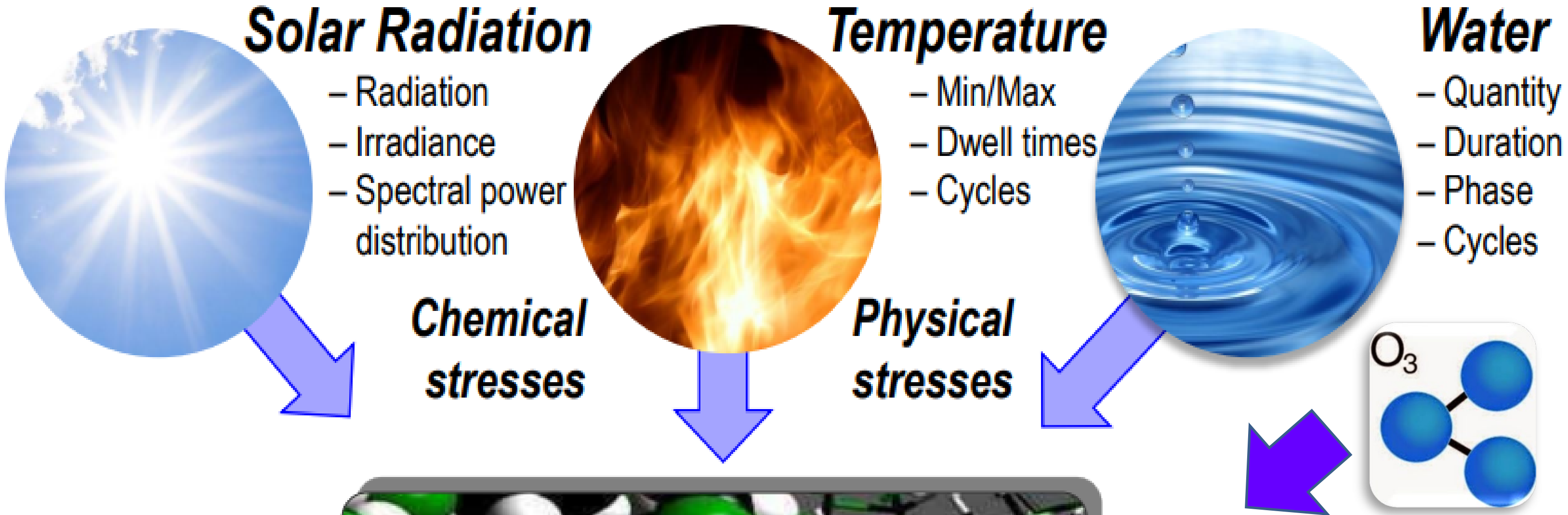



Sun Test XLS Weathering Chamber

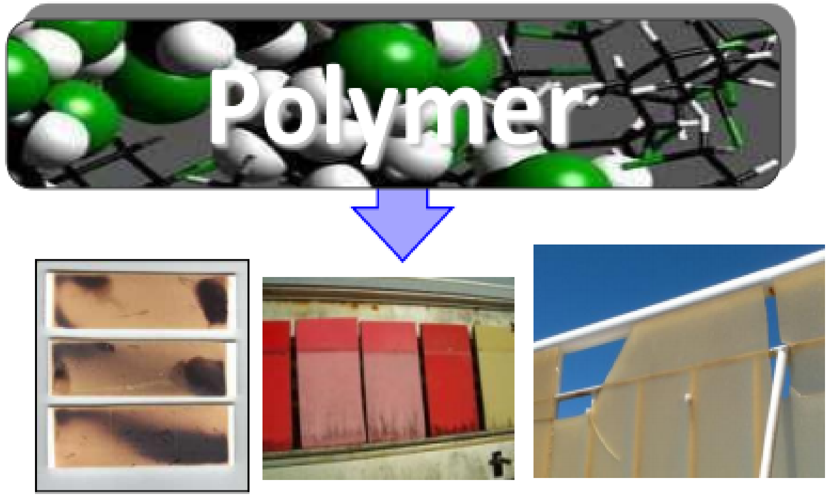



Test condition equivalent to a clear day on June 21, Miami Florida

# The primary weathering factors



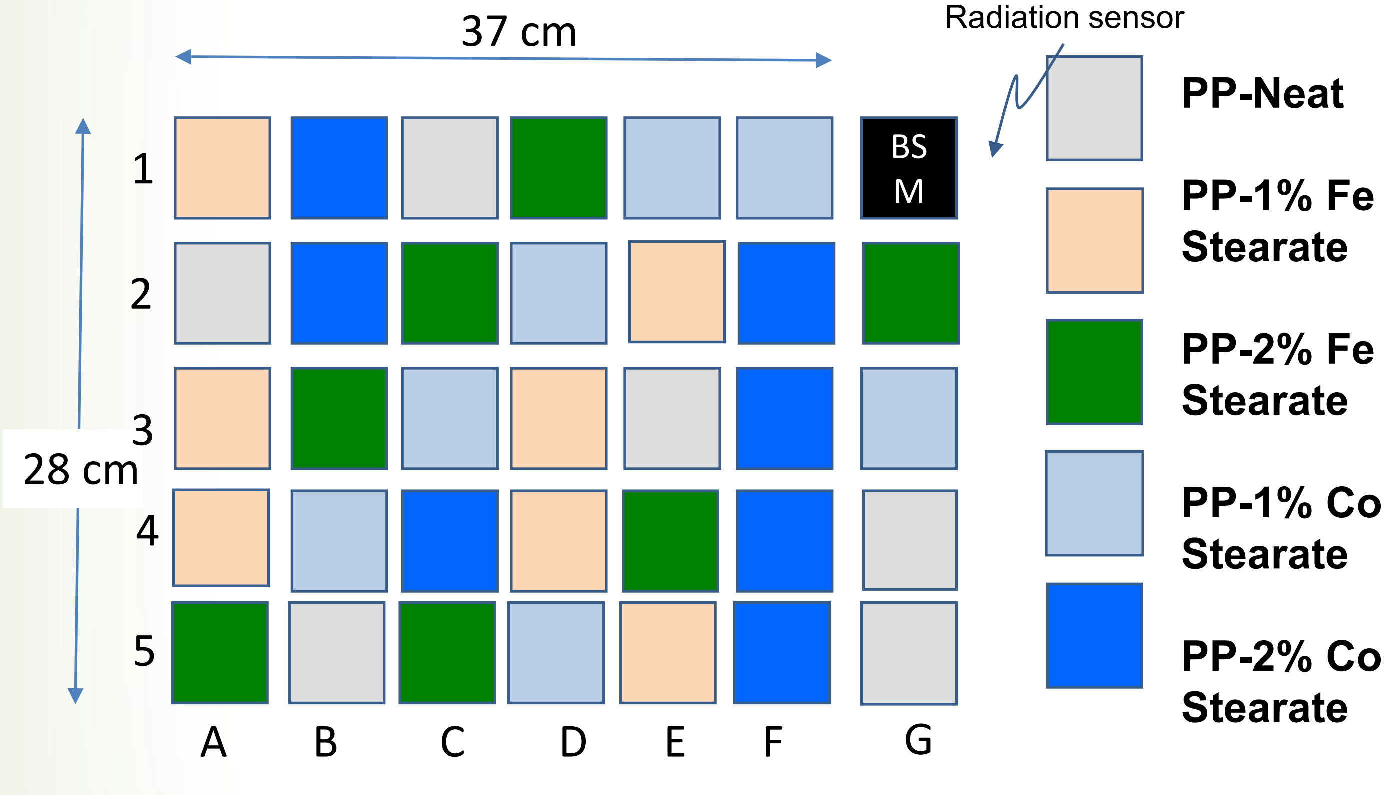

+ secondary factors (urban pollutants, acid rain, etc. …)




1. Chemical microscopic damage
2. Visual macroscopic damage

Synergy: “The combined effects are greater than the sum of the parts”

# Sample wafers and locations in the weathering chamber

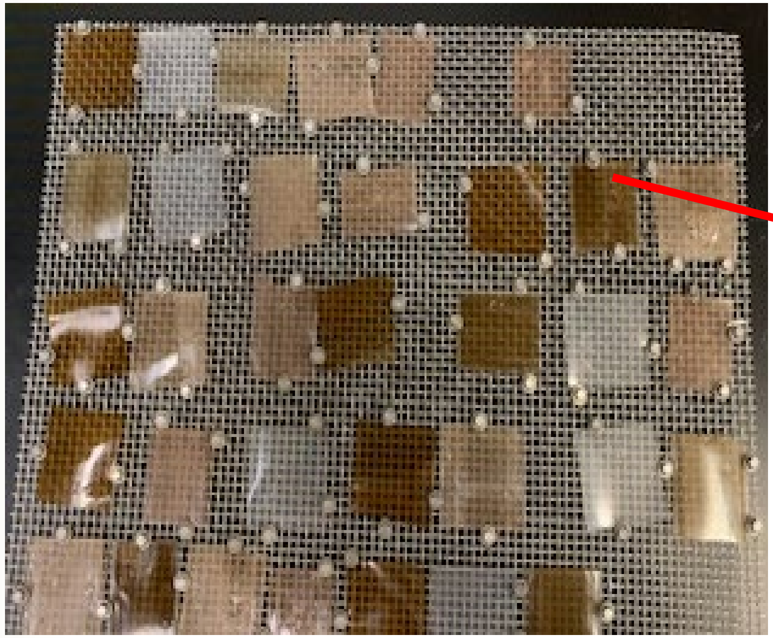



Test Samples

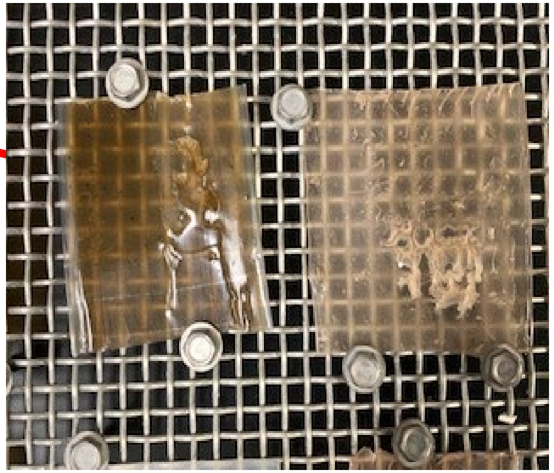
- **35 sample position**
- **7** replicates each
- Light control – Neat PP in chamber
- Dark control – 3 of each kept in dark locker
- All analysis in replicates

# Sample wafers and locations in the weathering chamber.

Sample Wafer holding tray

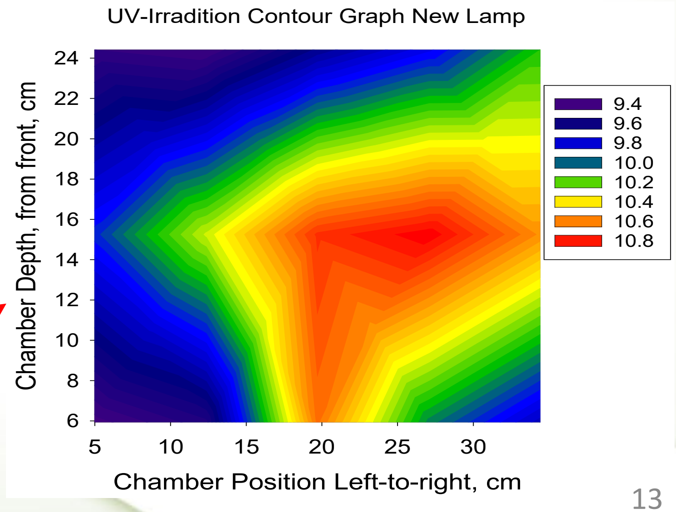


**Random number generator used to locate sample positions**



Wafer held in position with stainless steel screws

| NEW LAMP Irradiation | mW/cm2 |
|---|---|
| Average | 10.00 |
| Standard Deviation | ±0.50 |



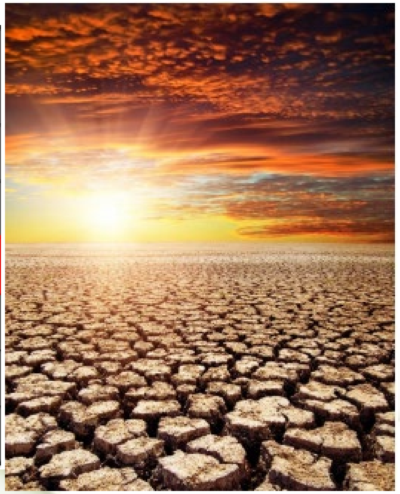

Samples are located at selected spots in the weathering chamber where the light intensity is known.

# Operating conditions

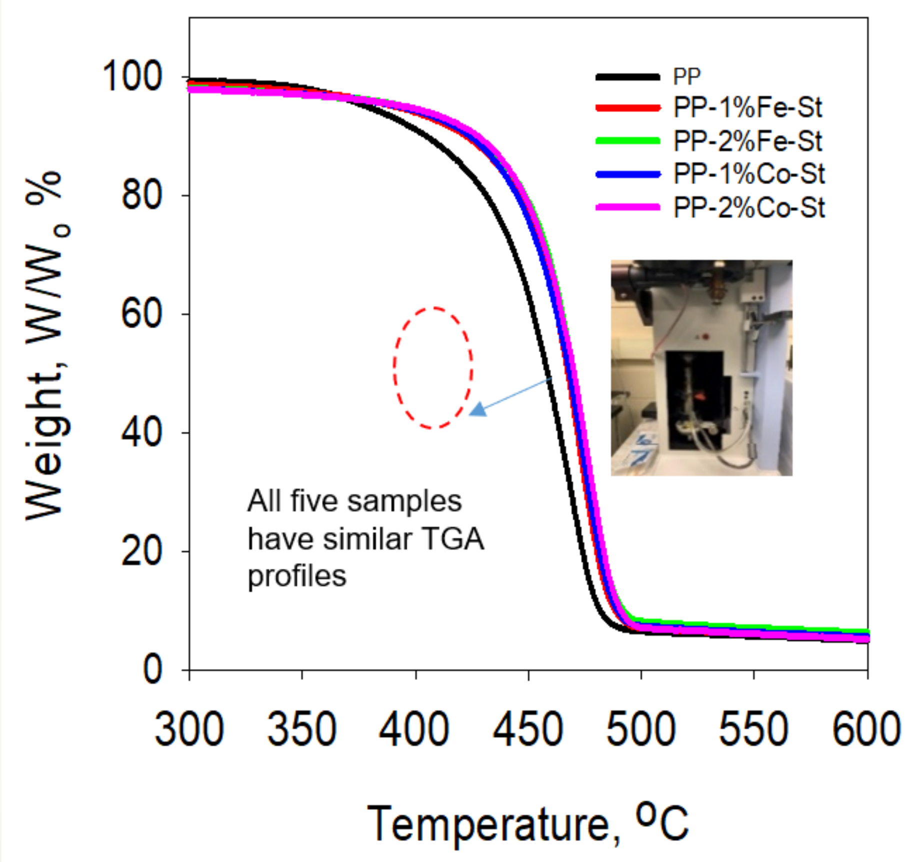
| Parameter | Condition |
|---|---|
| A cycle of weathering | 120 min (sunshine: 108 min and rain: 12 min) |
| Humidity | 8-20% for Sunshine and over 60% for Rain |
| Solar light irradiation | 700 $W/m^2$ |
| Wavelength of solar light | 300-800 nm |
| Chamber Temperature | 33-37 $^oC$ |
| Black Substance Temperature | 65 $^oC$ |

June 21, clear day

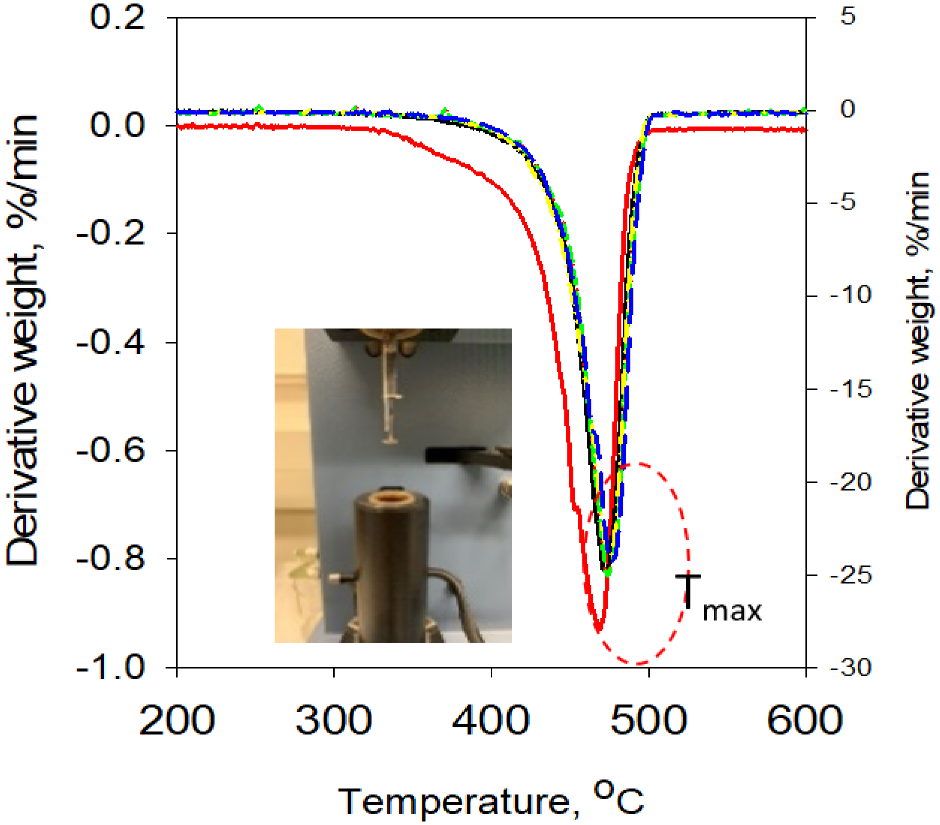
| Wavelength range | Arizona | Florida | Frankfurt | Barcelona | CIE No. 85 (Tab. 4) |
|---|---|---|---|---|---|
| nm | E ($W/m^2$) | E ($W/m^2$) | E ($W/m^2$) | E ($W/m^2$) | E ($W/m^2$) |
| 280-300 | 0.016 | 0.017 | 0.008 | 0.018 | 0.010 |
| **300-400** | **60** | **62** | **48** | **61** | **66** |
| 400-800 | 566 | 584 | 469 | 542 | 617 |
| 800-4000 | 420 | 387 | 350 | 373 | 434 |
| 280-4000 | 1046 | 1033 | 867 | 976 | 1117 |



# Thermogravimetric analysis of unaged PP with and without pro-oxidant additives

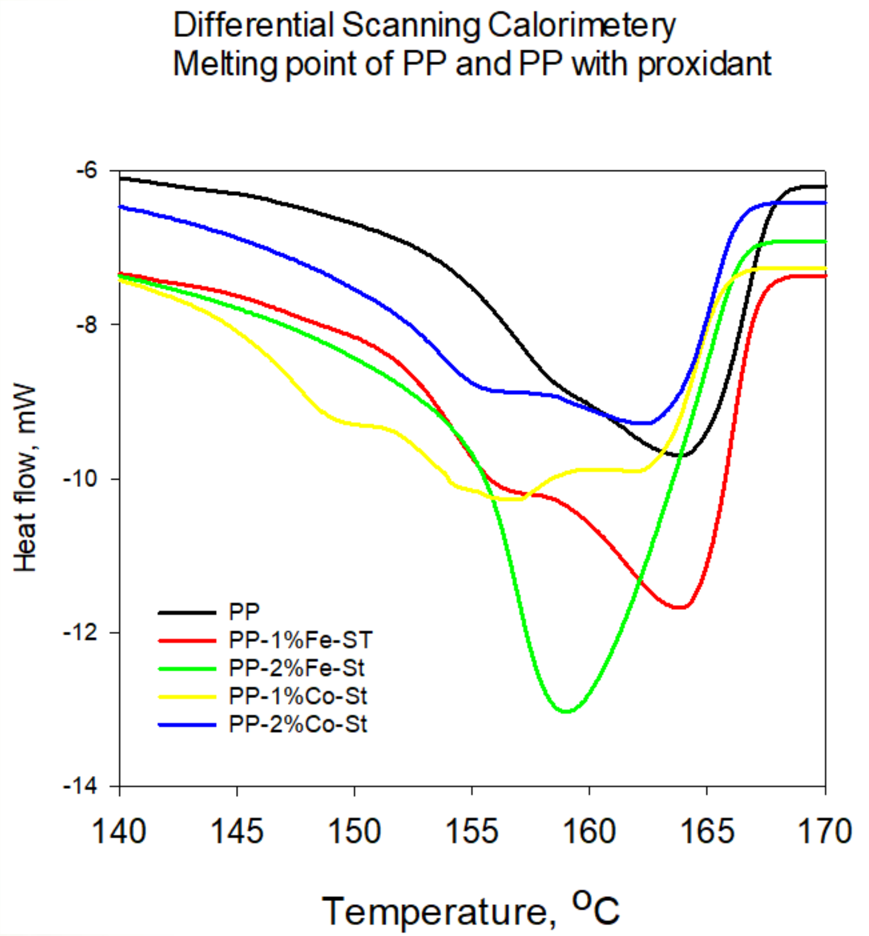


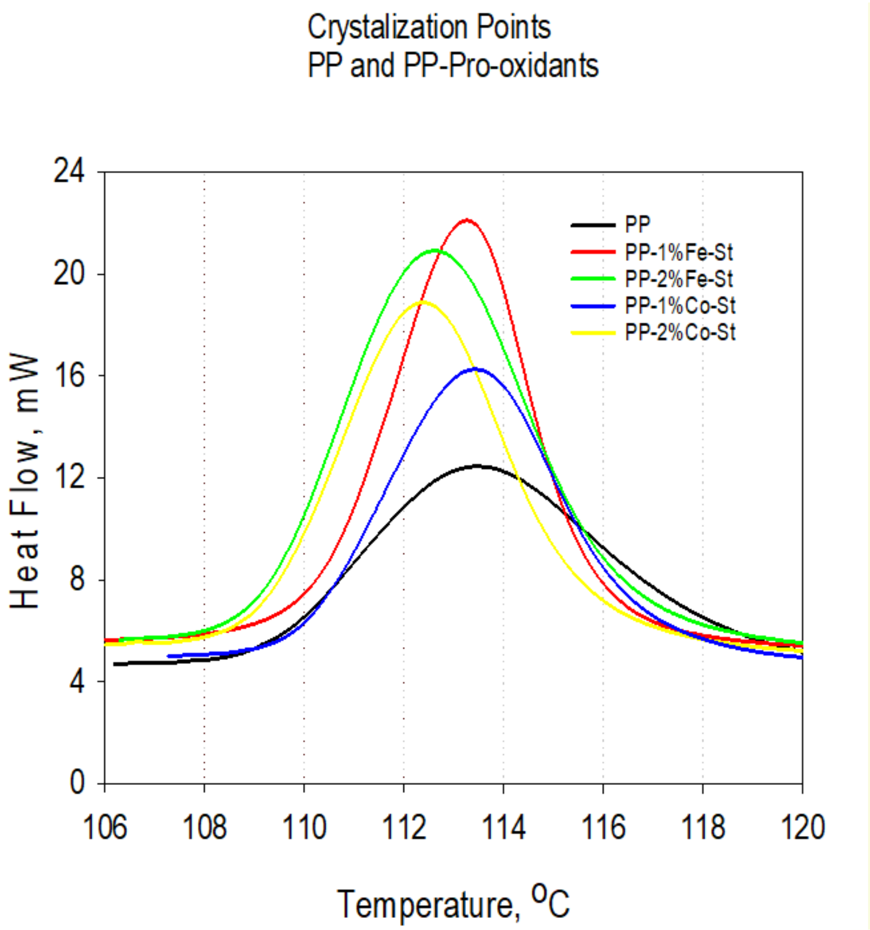

## Derivative thermogravimetry




DTG = rate of weight change = f(temp) thermal decompositions & physical and chemical characteristics

# Thermal Analysis unaged PP with and without pro-oxidant additive

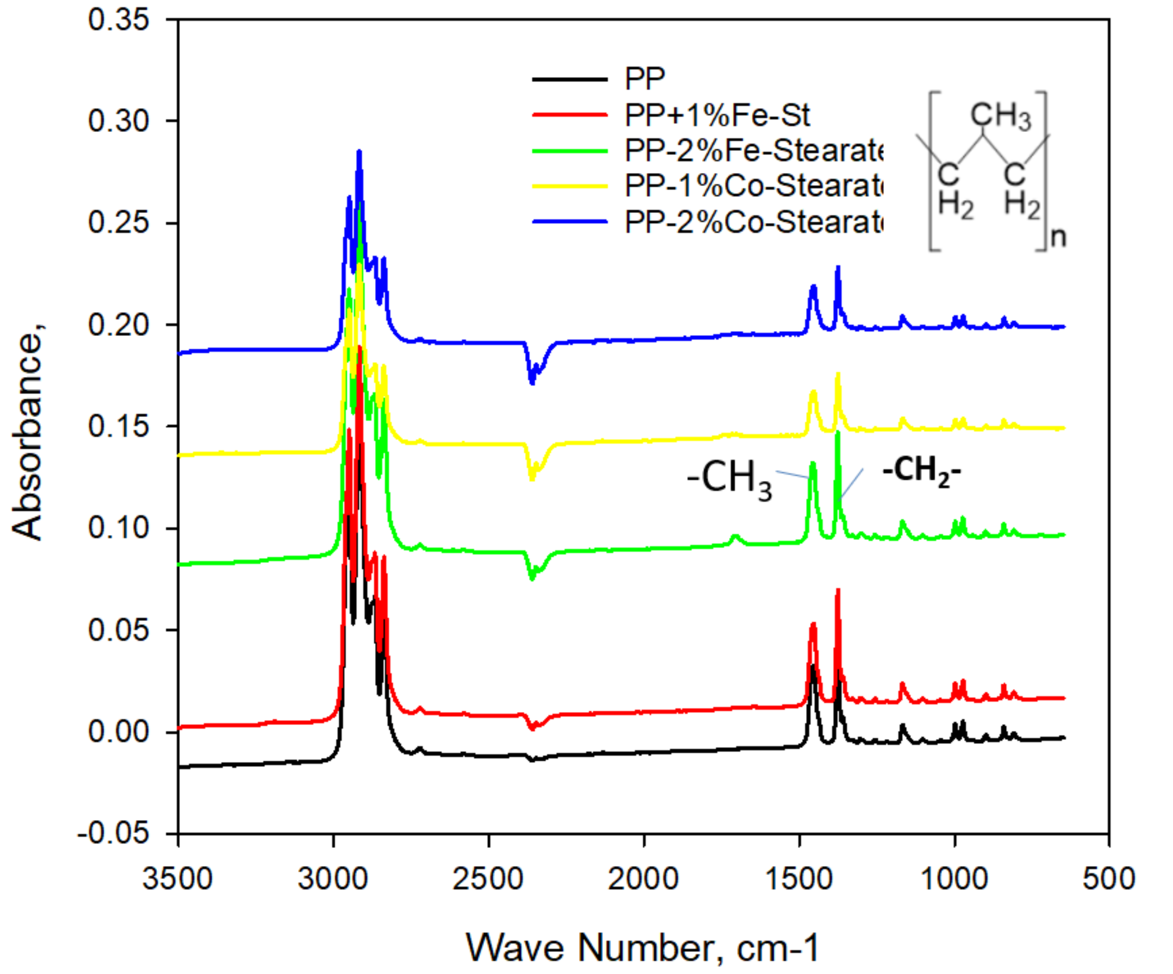


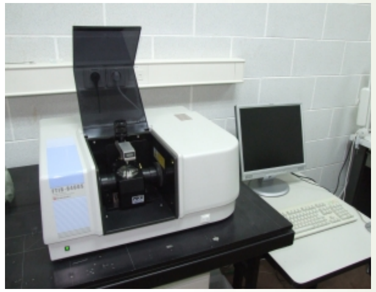




- Similar melting 160$^{o}$C. /crystallization temperatures 110 and 114$^{o}$C

# Fourier-transform infrared spectroscopy analysis surface chemistry

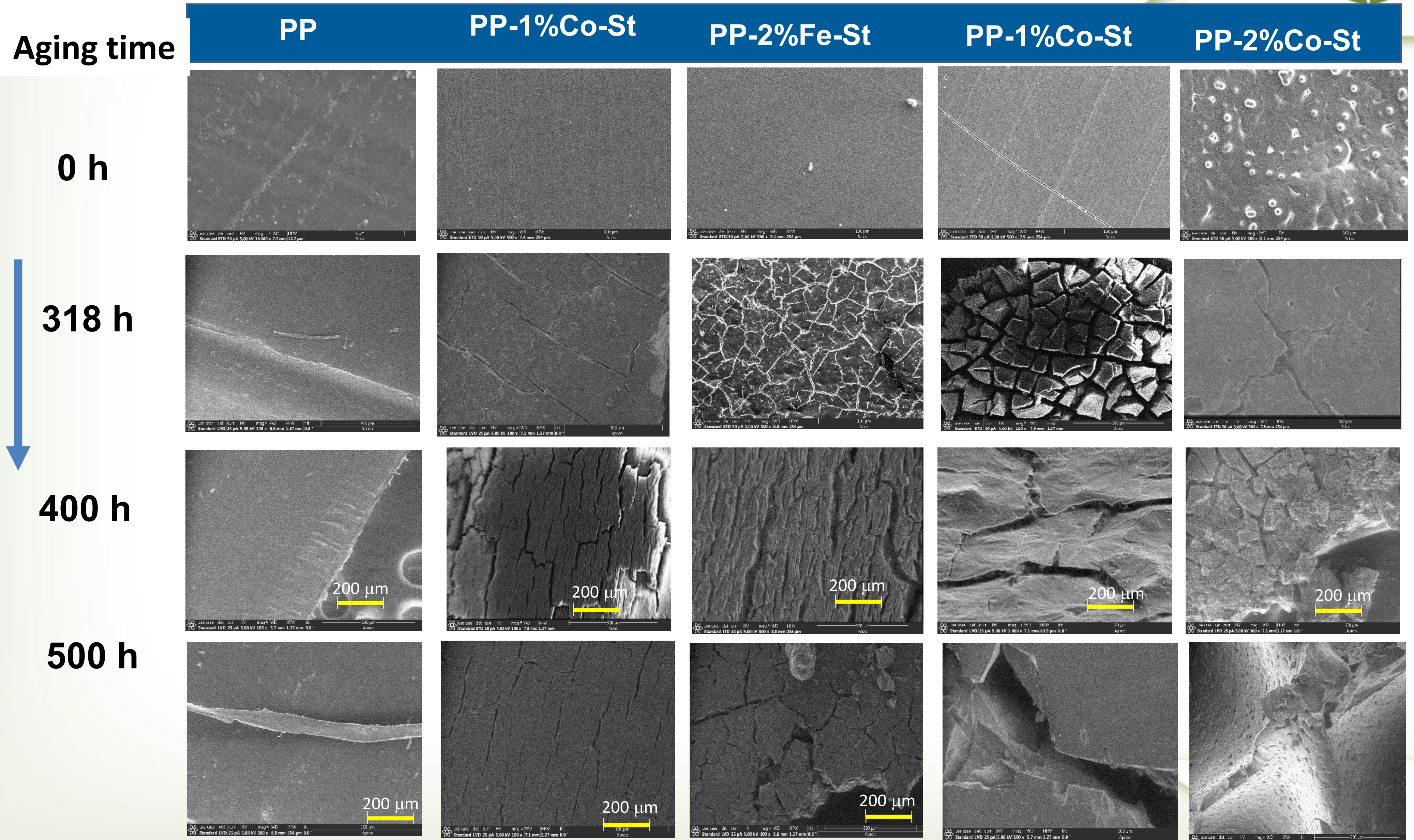
FTIR of PP and PP-Prooxidant additives



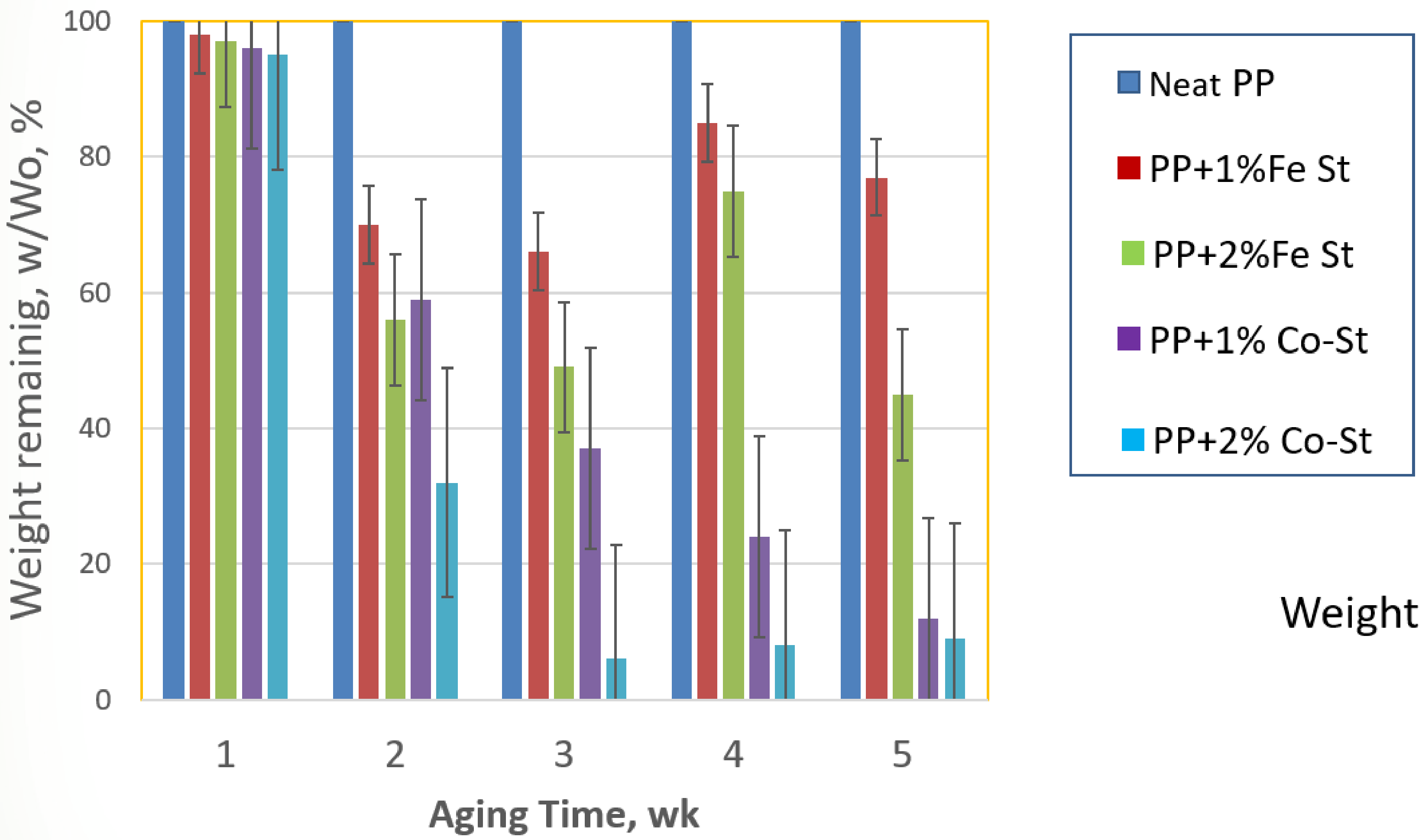



No difference in FTIR spectra of PP and PP with pro-oxidant filler→ similar chemical properties

# Scanning electron micrograph PP with and without PP-pro-oxidants at selected aging times

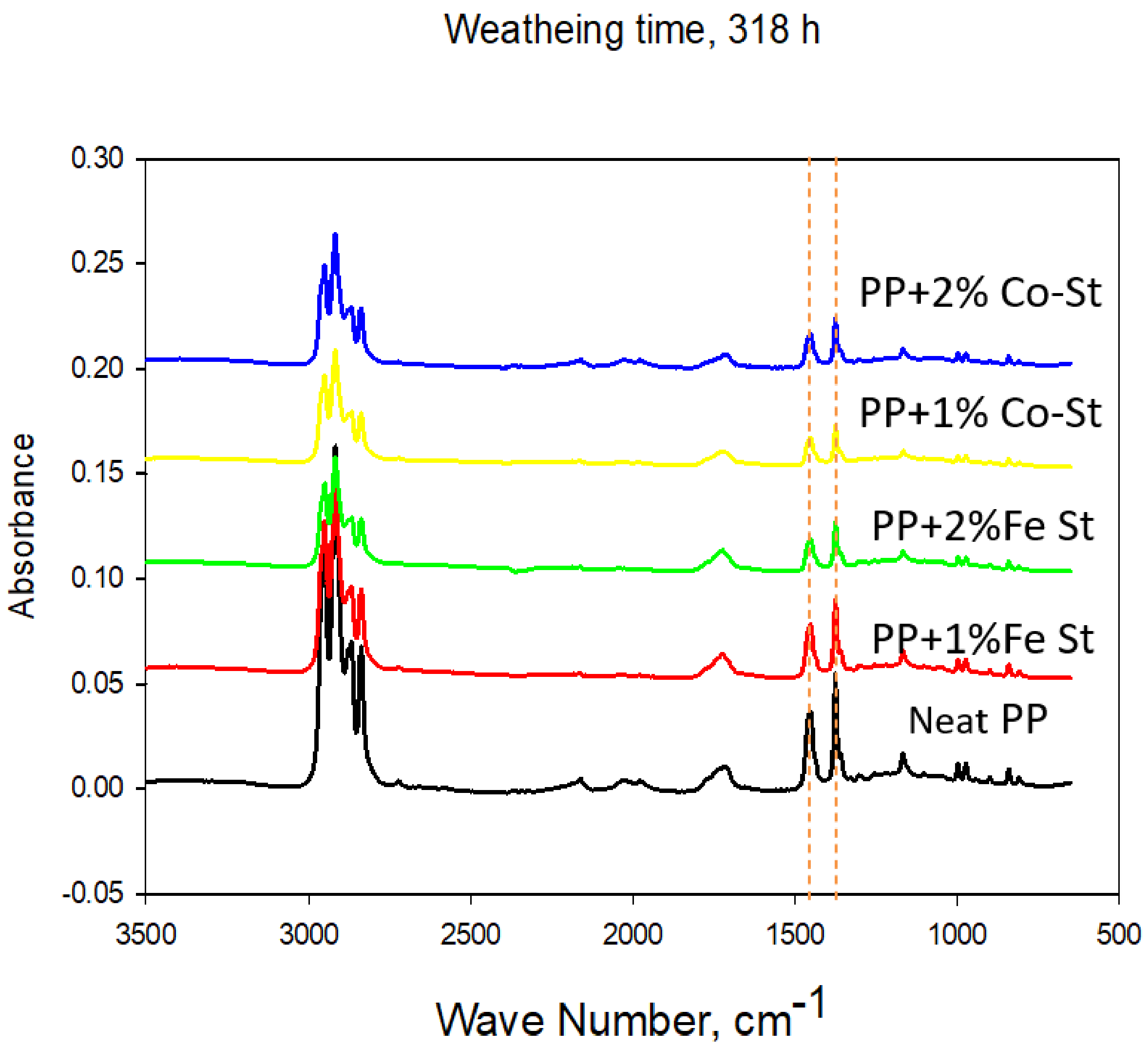


# Accelerated aging of PP with pro-oxidant



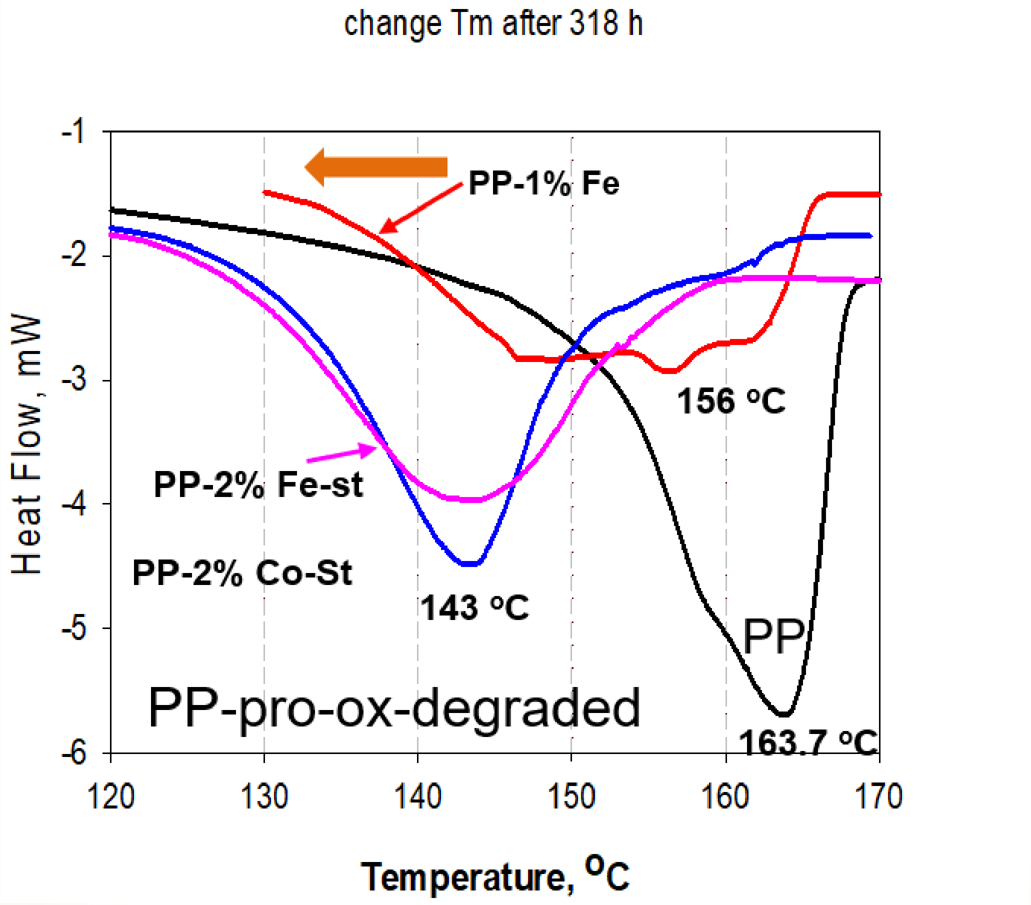

Weight loss depends

# FT IR of aged polymers

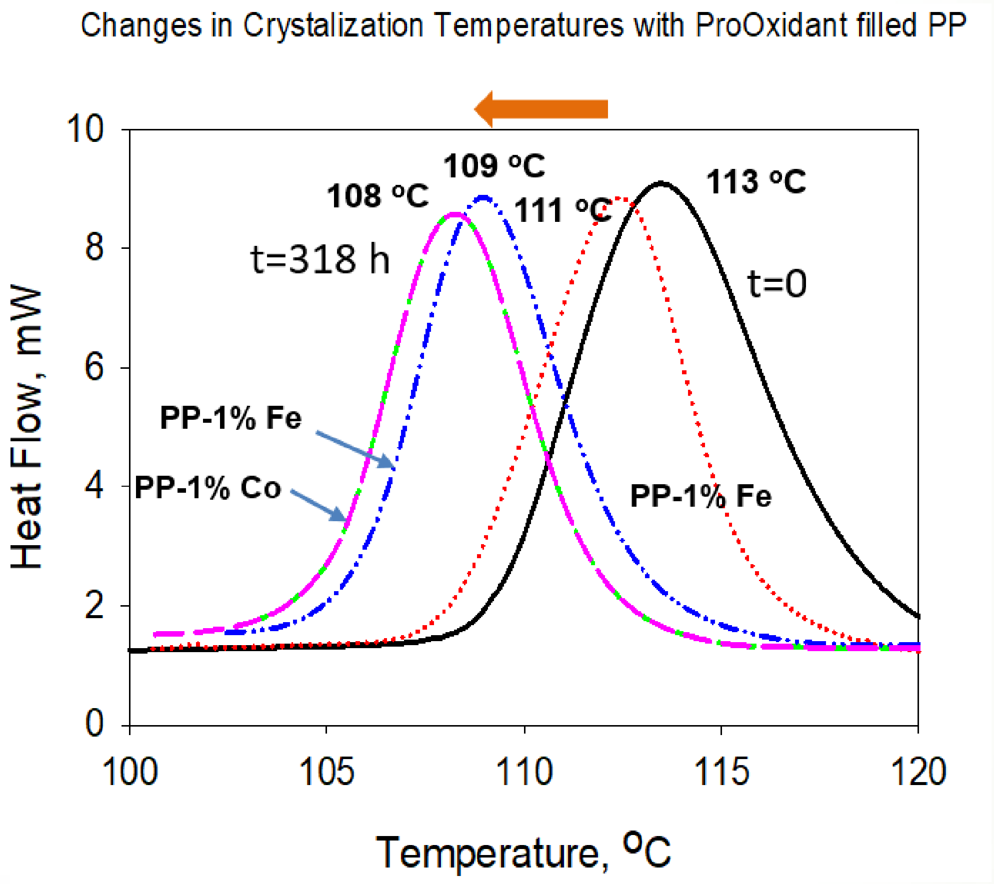


# Differential scanning calorimetry

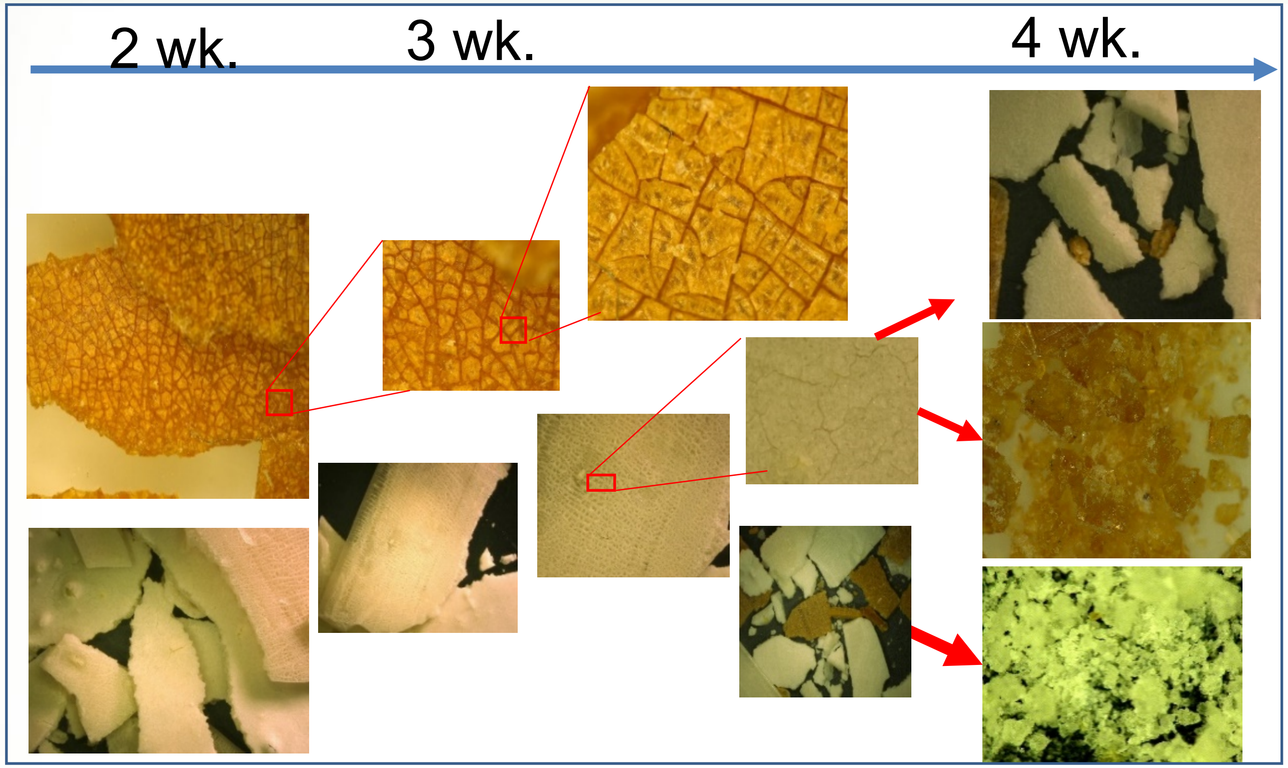
**Melting point decreases after 318 h aging**



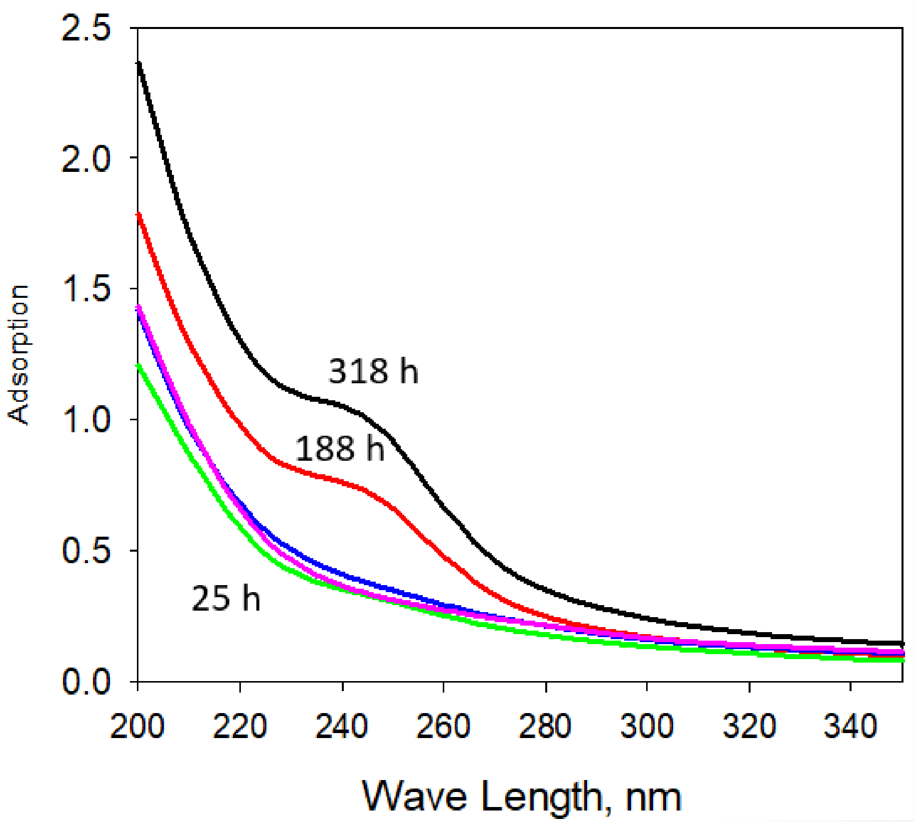

**Crystallization Temp. drops after 318 h aging**



# PP degradation and wash water analysis

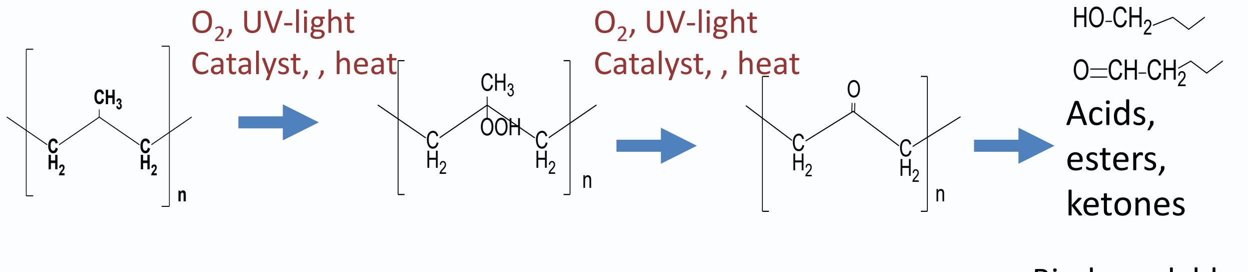



Digital images showing stages of PP degradation



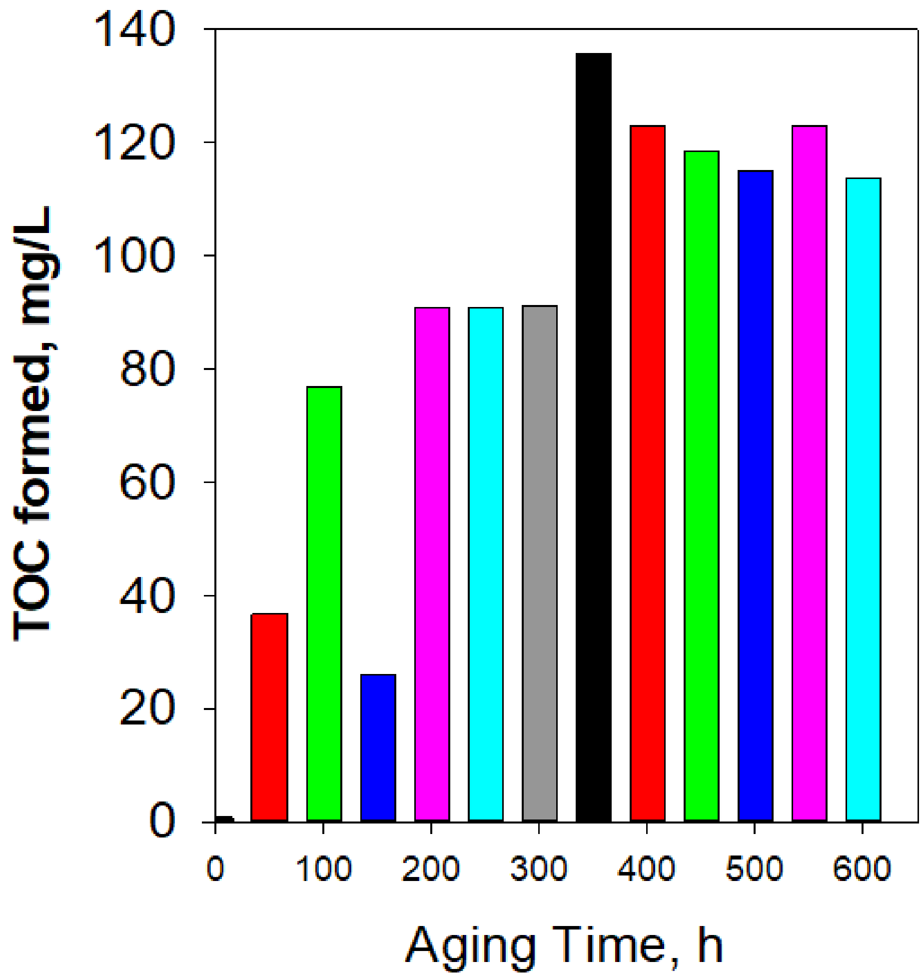

Wash-water analysis show absorbance at 254 nm with aging time indicate pp degradation products that are water soluble, could be biodegradable

# Proposed environmental degradation mechanism




Mechanism of radical oxidation of polypropylene

Pro-oxidant promote formation of free radicals (e.g. Hydroperoxide) by photo degradation breaks the polymer chain



# Tensile Strength Analysis of PP and prooxidant added PP

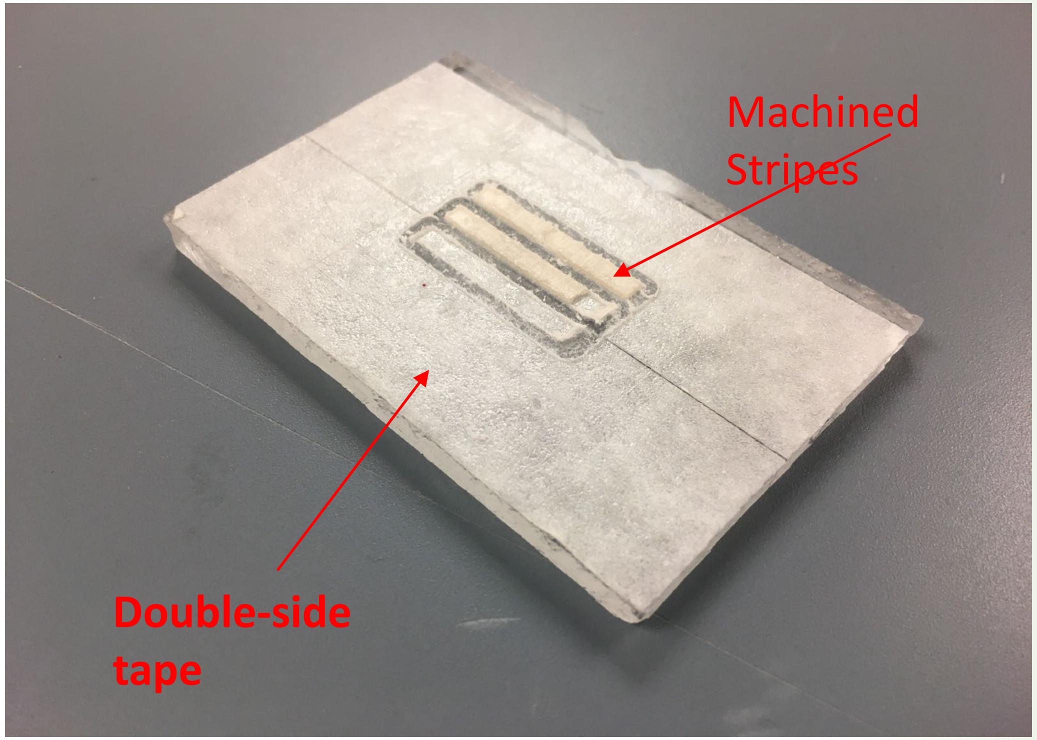
## Sample Processing

- Ionic bond + laser machining
  glue bonding is good
  sample size programable
  laser burns the polymer

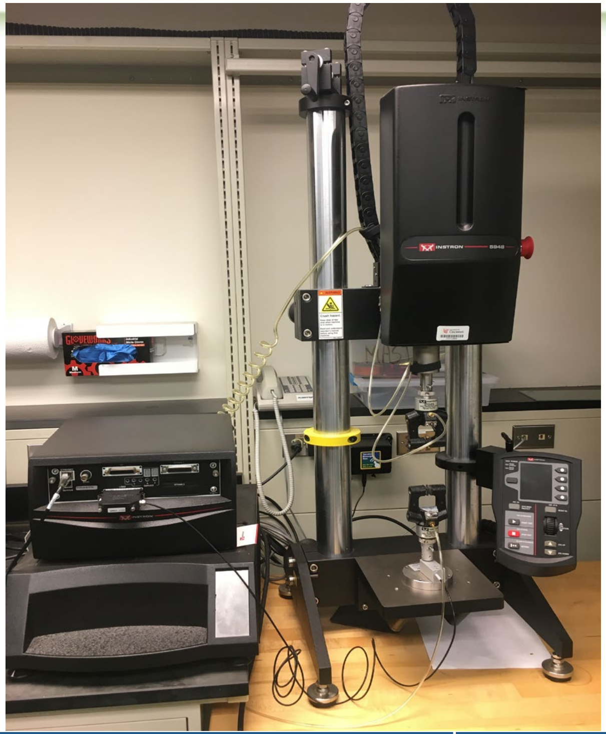
- Micro-milling machining
  taped on a stage
  sample size programable
  mechanical machining

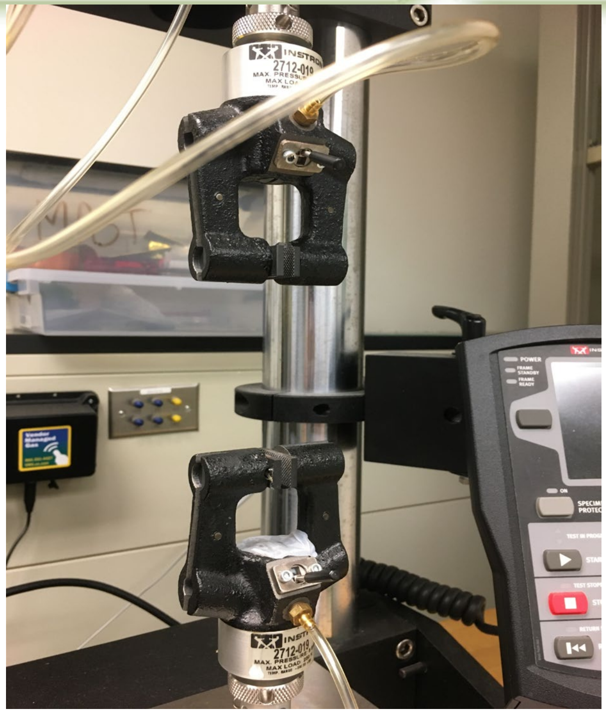

# Micro-milling of LDPE





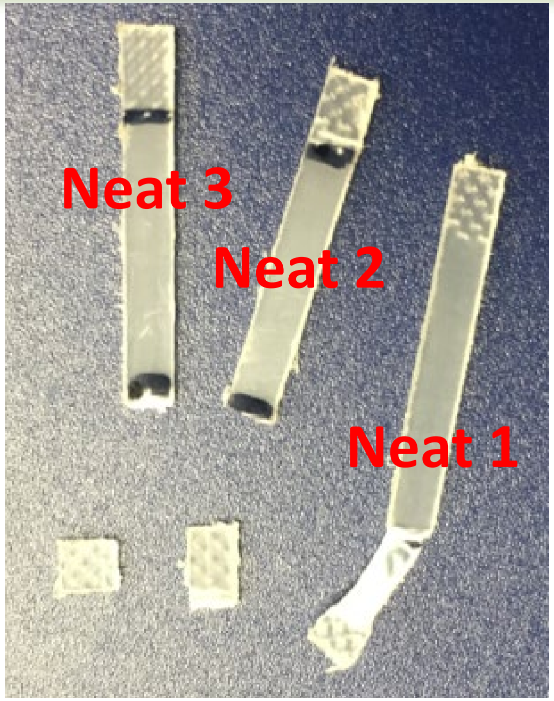
# Mechanical Testing of PP



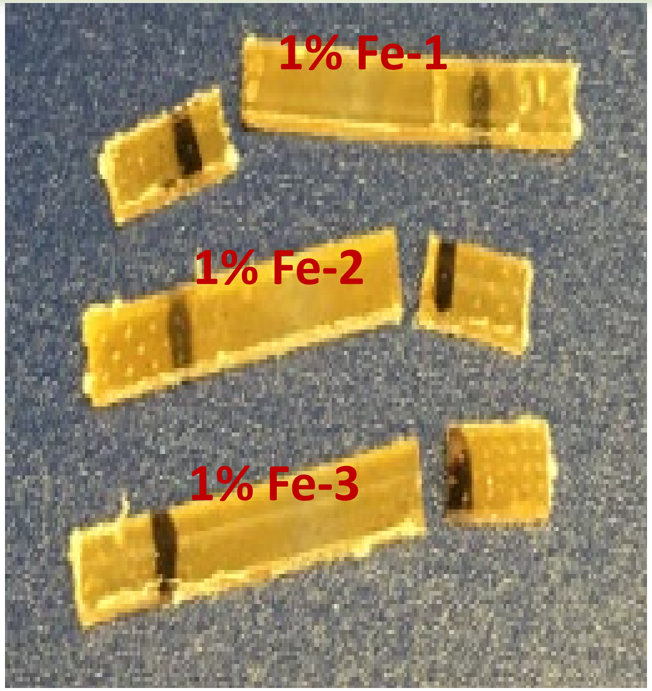


| Sample ID | Size (mm) | Strain Rate (mm/min) |
|---|---|---|
| Neat 1 | 4x1x25 | 0.5 |
| Neat 2 | 4x1x25 | 1 |
| Neat 3 | 4x1x25 | 1 |
| 1% Fe-1 | 4x1x25 | 1 |
| 1% Fe-2 | 4x1x25 | 1 |
| 1% Fe-3 | 4x1x25 | 1 |

# Tensile test strip samples

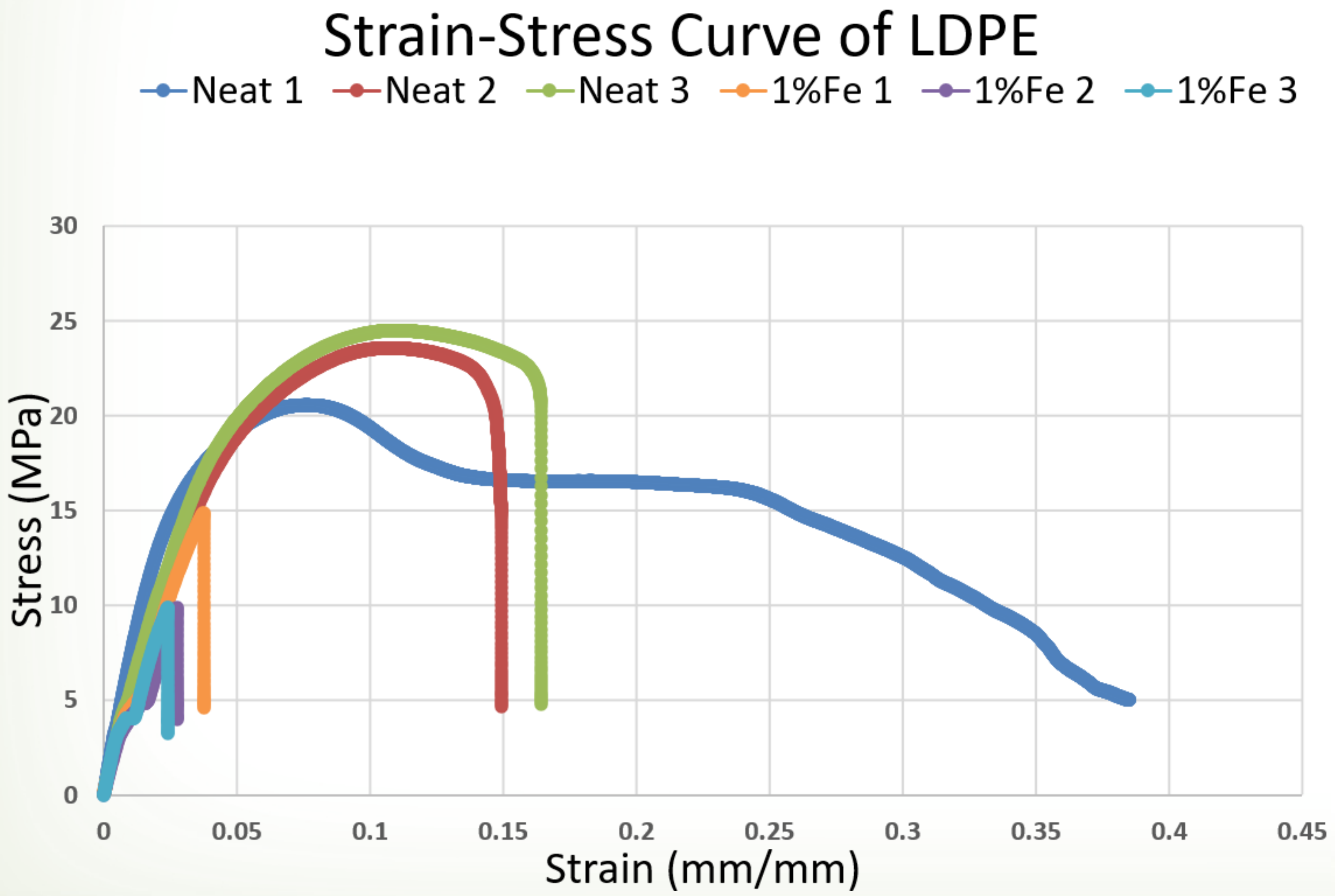



Neat PP samples strips




PP with Fe-stearate additives samples strips

# Tensile strength test result




- Neat LDPE has better modulus, break strain, and ultimate tensile stress
- The addition of Fe and Co makes LDPE brittle
- As more Fe is added to the system, LDPE becomes more brittle

# Conclusion

- Neat PP showed little or no changes, PP-with pro-oxidant filler degraded rapidly.
- Pro-oxidant additives in PP embrittle, crack and break into pieces and powder within two weeks of weathering.
- Reduction in melting and crystallization points indicate  chain breaking and de-polymerization of PP
- Degradation rate follows Co 2%> Fe 2%> Co 1%> Fe 1%
- UV spectroscopy shows water samples contain degradation products that are water soluble, could be potential biodegradable
- Washed water analysis following filtration using UV-vis spectroscopy and  total organic carbon analysis show increase in dissolved organic product from the degraded polypropylene.
- Changes in the mechanical properties of polymers due to pro-oxidants, requires more studies.

# Disclaimer

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**Thank you**