



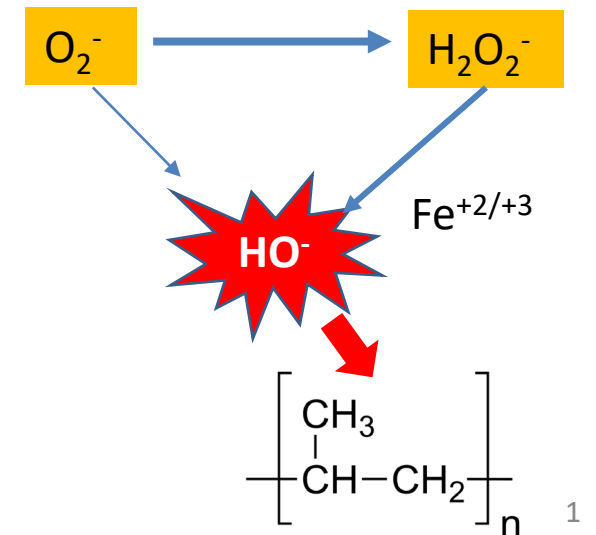
Accelerating Polymer Degradation using Pro-oxidant Additives

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Why is plastic a problem?



- 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

Sustainable Solution

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

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

Plastics Pollution a Global Challenge

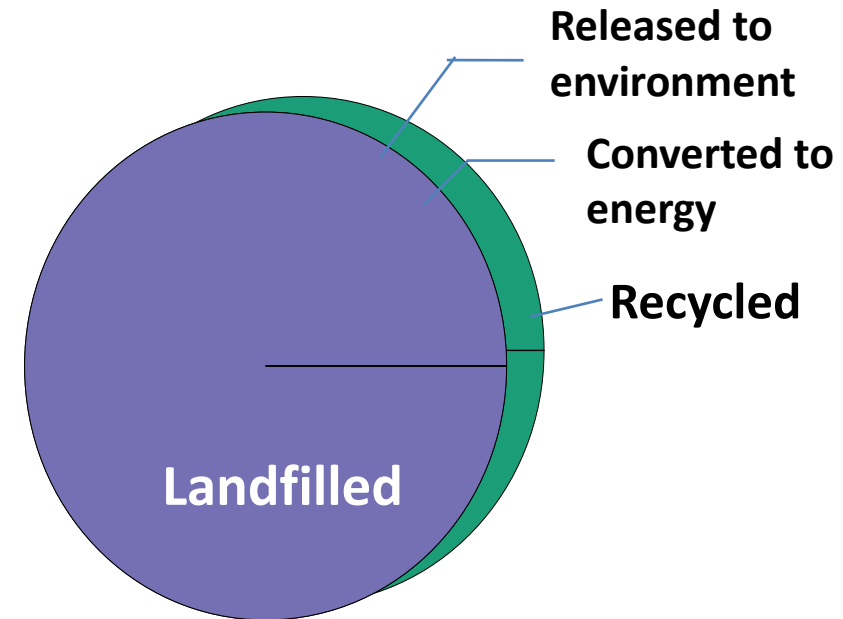


Essential: Plastics are considered to have made the modern world possible. (used for packaging, construction materials, automotive, electrical devices)

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.

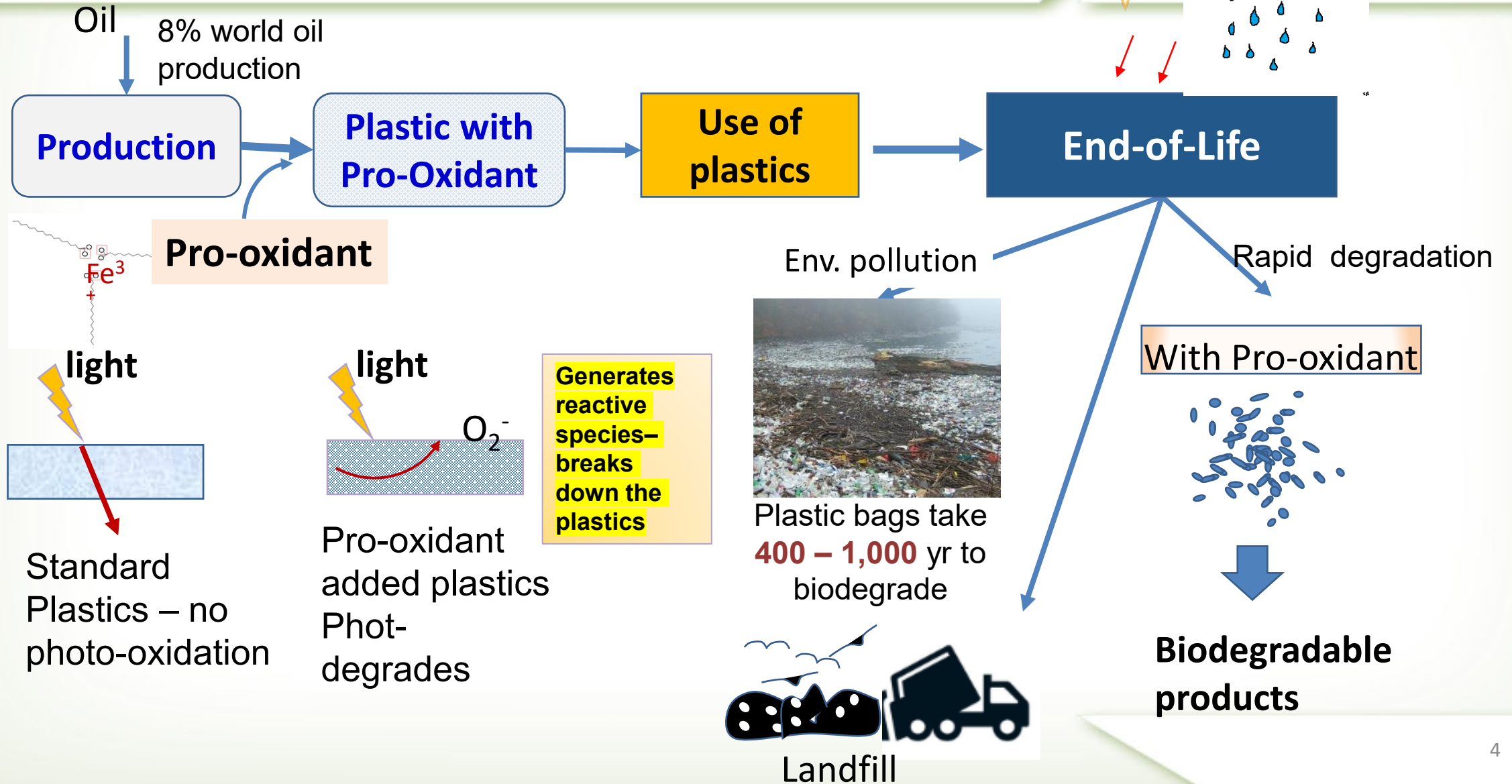
End-of-life of plastics



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

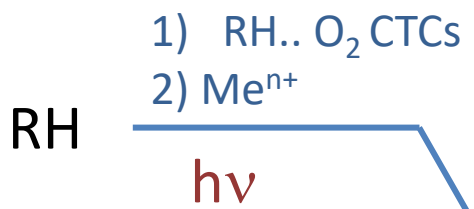
Eliminate persistence of plastics by adding a safe pro-oxidant to make a low-cost biodegradable plastic

Life cycle stages of plastics

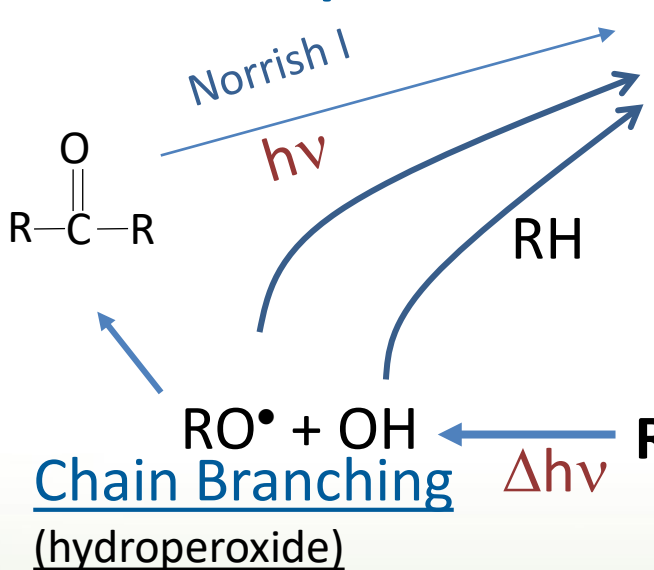


Photooxidation of polymers: Chain and Photochain Mechanism

1. Direct Initiation



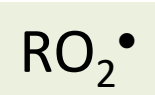
2. Oxidative Impurities



O_2 (absorption)



Propagation



Termination

Inert O_2



CTC – charge transfer complexes

Research Objectives



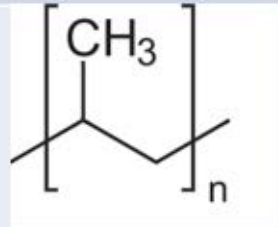
Hypothesis: Adding *pro-oxidants* significantly accelerates photo-degradation of plastics and become biodegradable

- 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



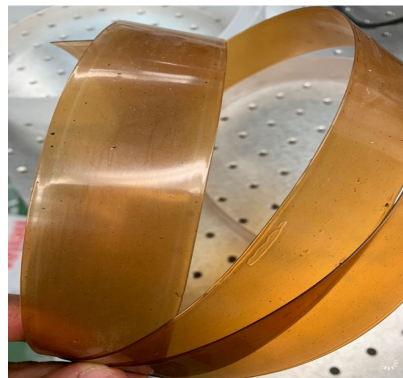
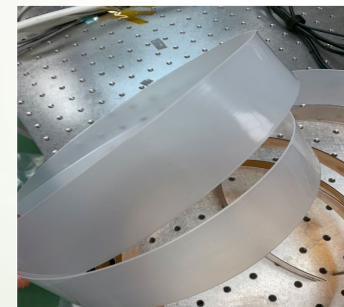
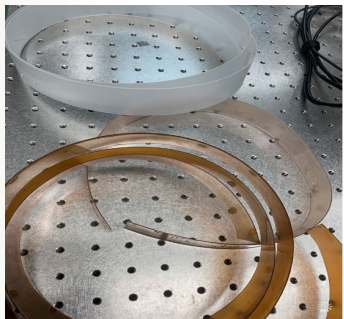
PP beads



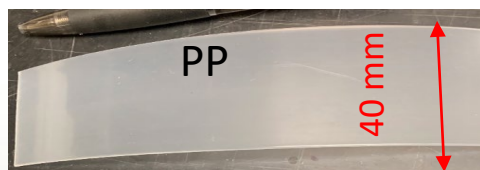
Melt PP Mix with Pro-oxidants



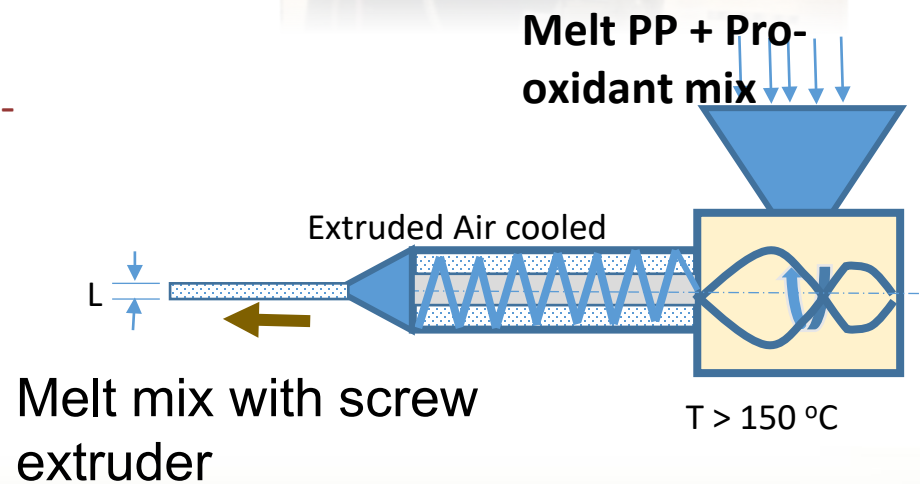
Screw extrusion



PP+2%Fe-stearate

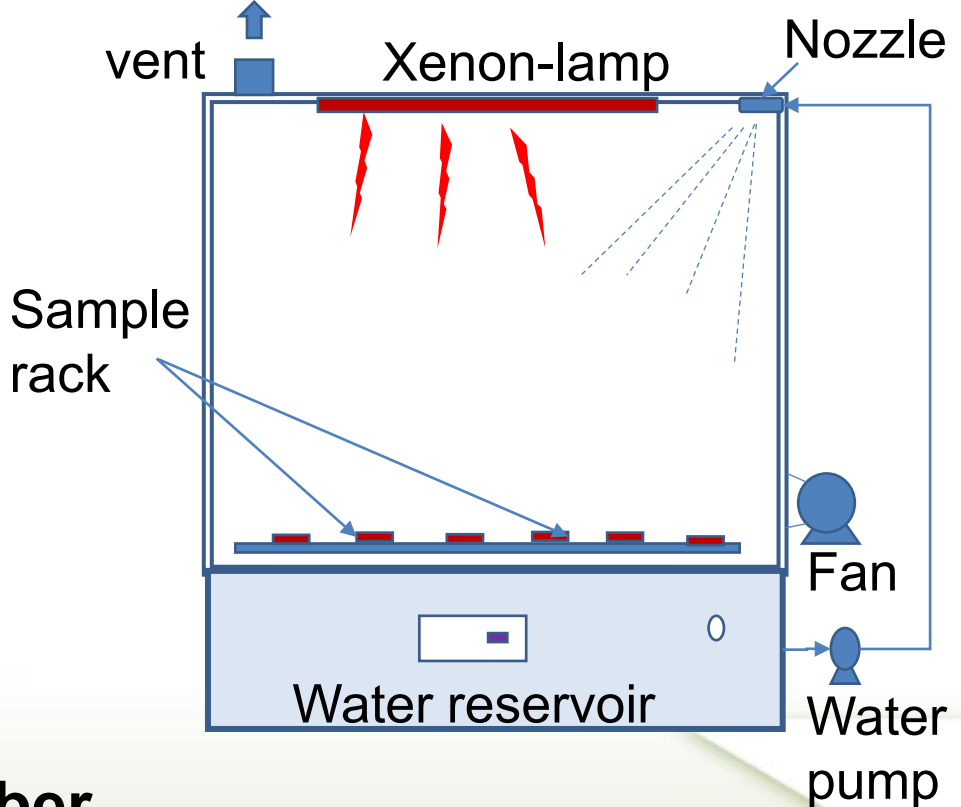
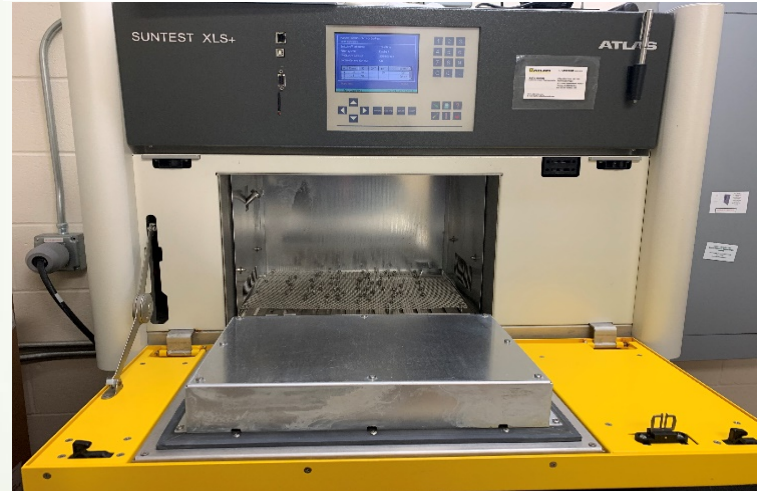
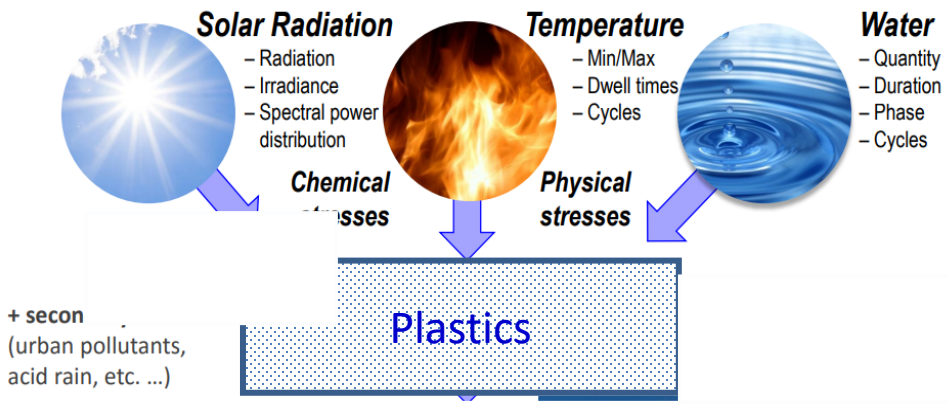


Thickness 1 mm



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

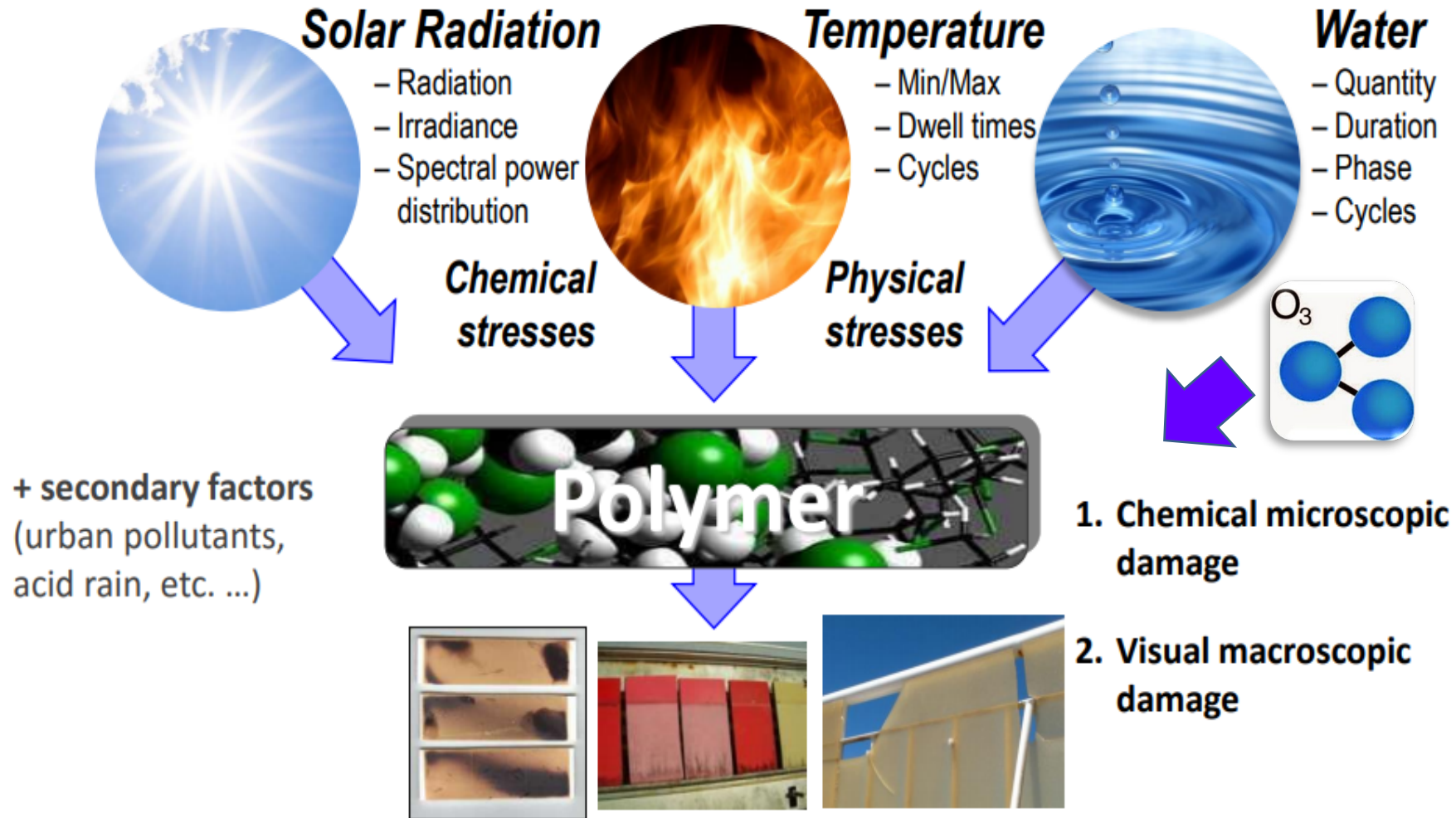
Parameter	Condition
A cycle of weathering	120 min (sunshine: 108 min, rain: 12 min)
Humidity	8-20% for sunshine and over 60% for rain
Solar light irradiation	700 W/m ²
Wavelength of solar light	300-800 nm
Chamber temperature	33-37 °C
Black substance temperature	65 °C



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

Sun Test XLS Weathering Chamber

The primary weathering factors

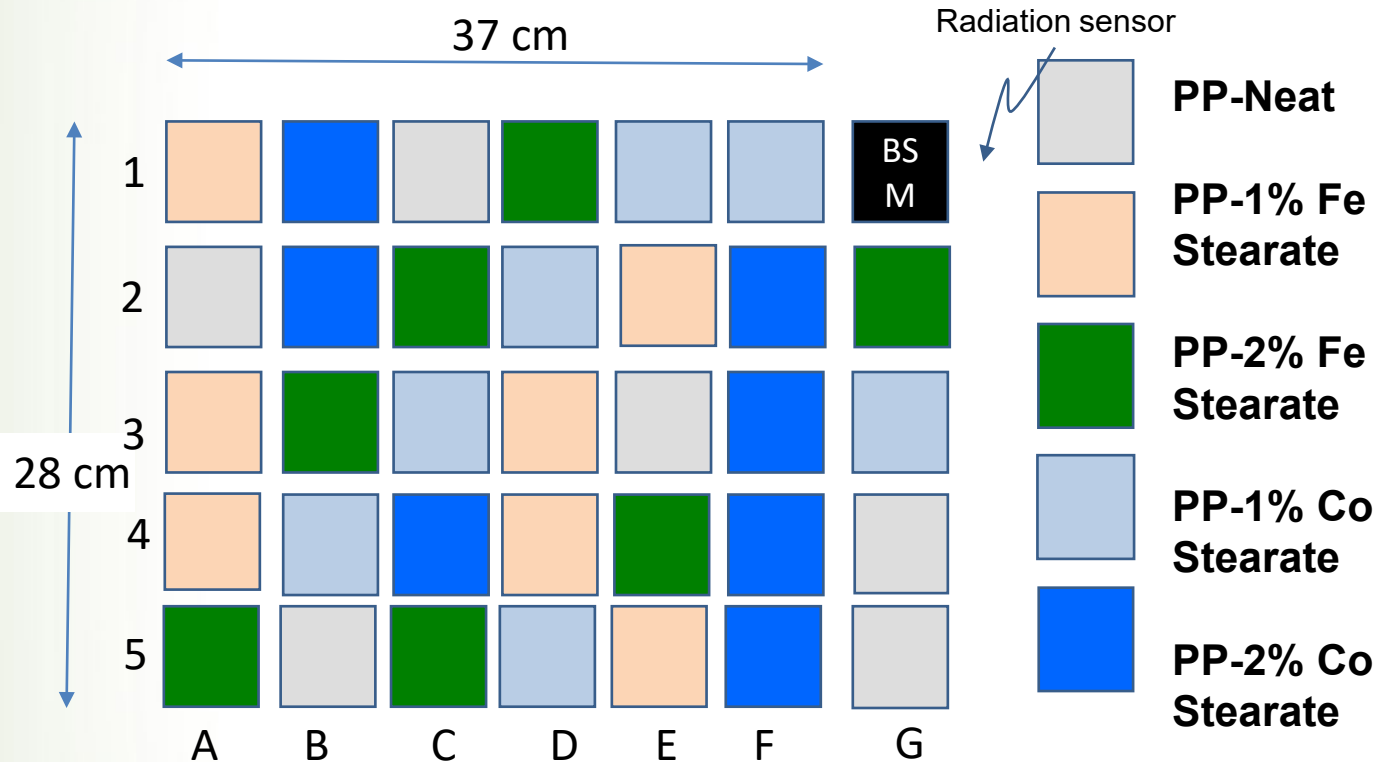


Synergy: "The combined effects are greater than the sum of the parts"

Sample wafers and locations in the weathering chamber



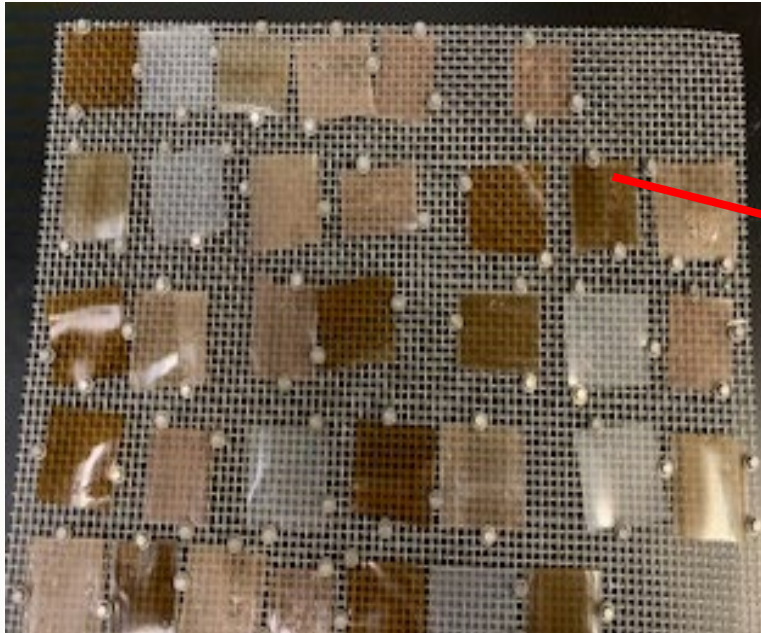
Test Samples



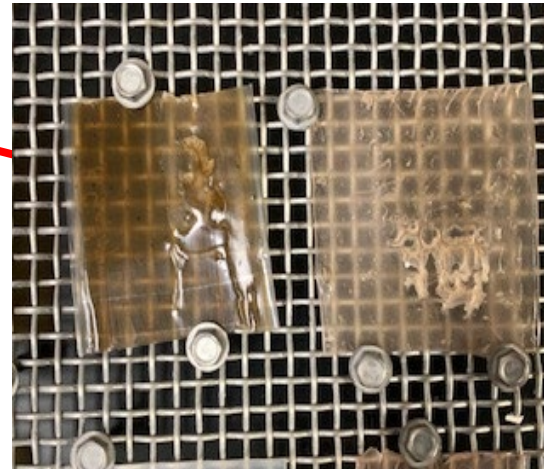
- **35 sample position**
- **7 replicates each**
- Light control – Neat PP in chamber
- Dark control – 3 of each kept in dark locker
- All analysis in replicates

Sample wafers and locations in the weathering chamber.

Sample Wafer holding tray



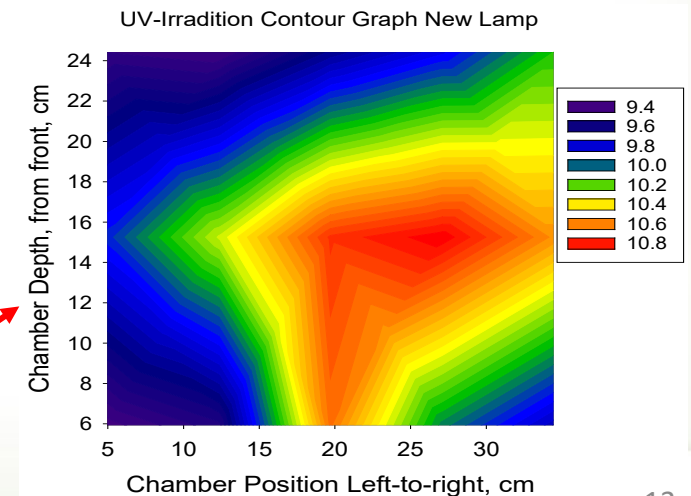
Random number generator used to locate sample positions



Wafer held in position with stainless steel screws

NEW LAMP Irradiation	mW/cm ²
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



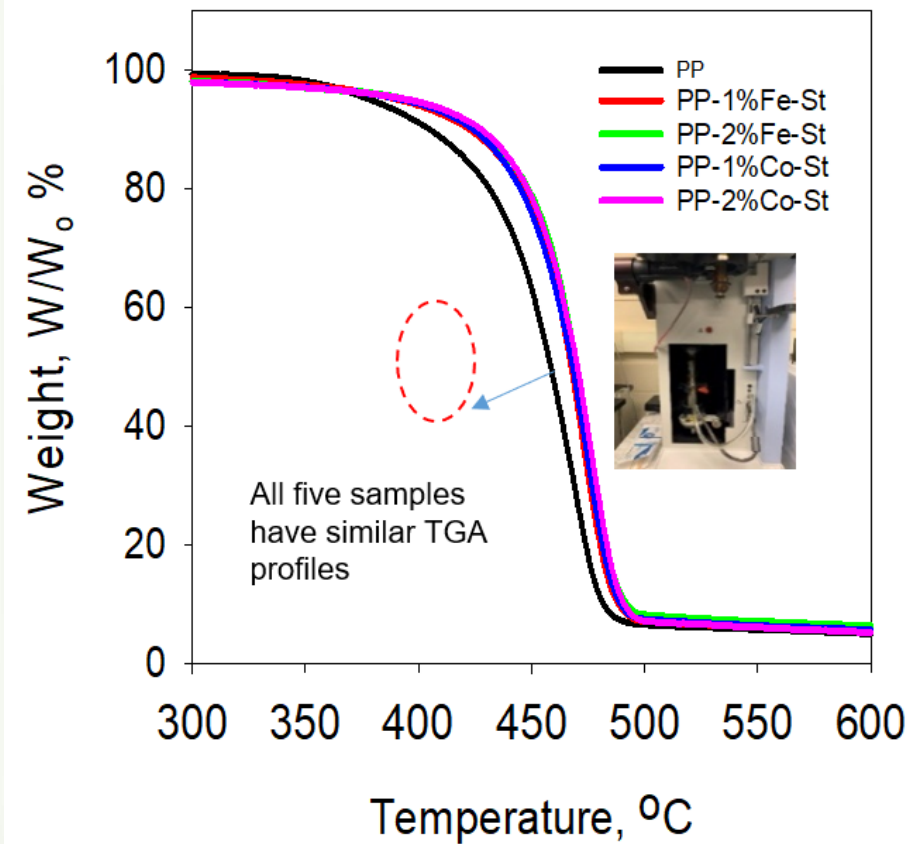
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Wavelength of solar light	300-800 nm
Chamber Temperature	33-37 °C
Black Substance Temperature	65 °C

June 21, clear day

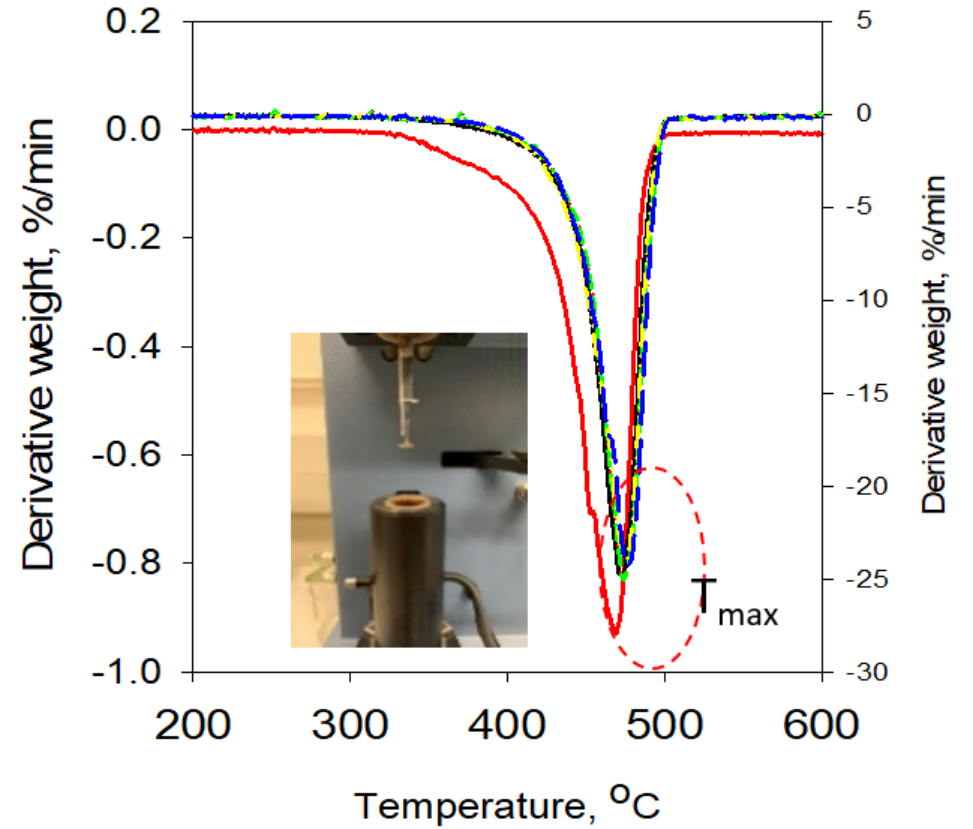
Wavelength range	Arizona	Florida	Frankfurt	Barcelona	CIE No. 85 (Tab. 4)
nm	E (W/m ²)	E (W/m ²)	E (W/m ²)	E (W/m ²)	E (W/m ²)
280-300	0.016	0.017	0.008	0.018	0.010
300-400	60	62	48	61	66
400-800	566	584	469	542	617
800-4000	420	387	350	373	434
280-4000	1046	1033	867	976	1117



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



Derivative thermogravimetry

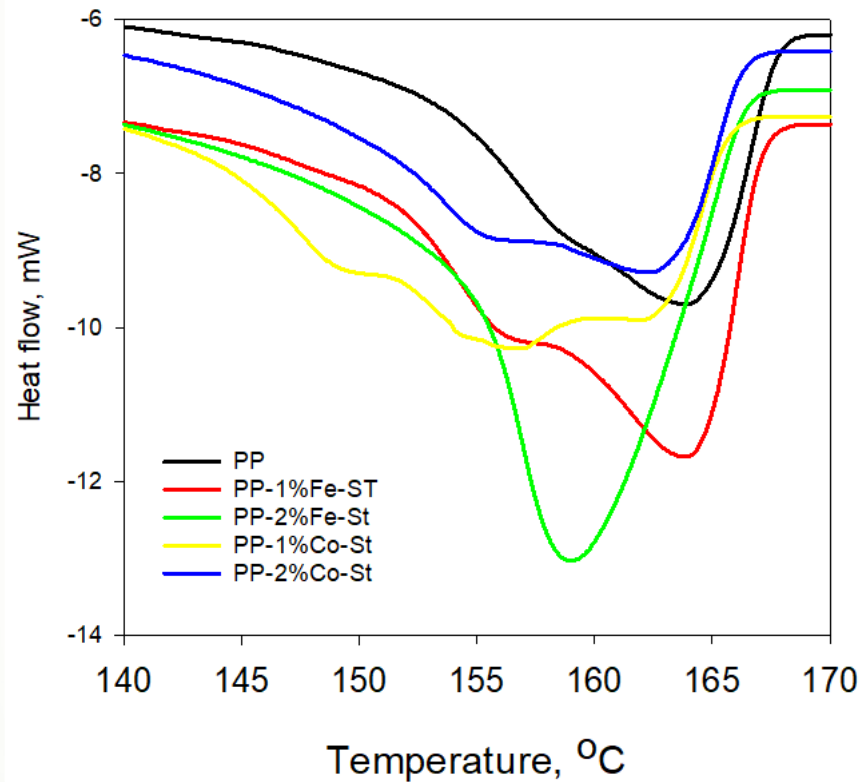


DTG = rate of weight change = $f(\text{temp})$ thermal decompositions & physical and chemical characteristics

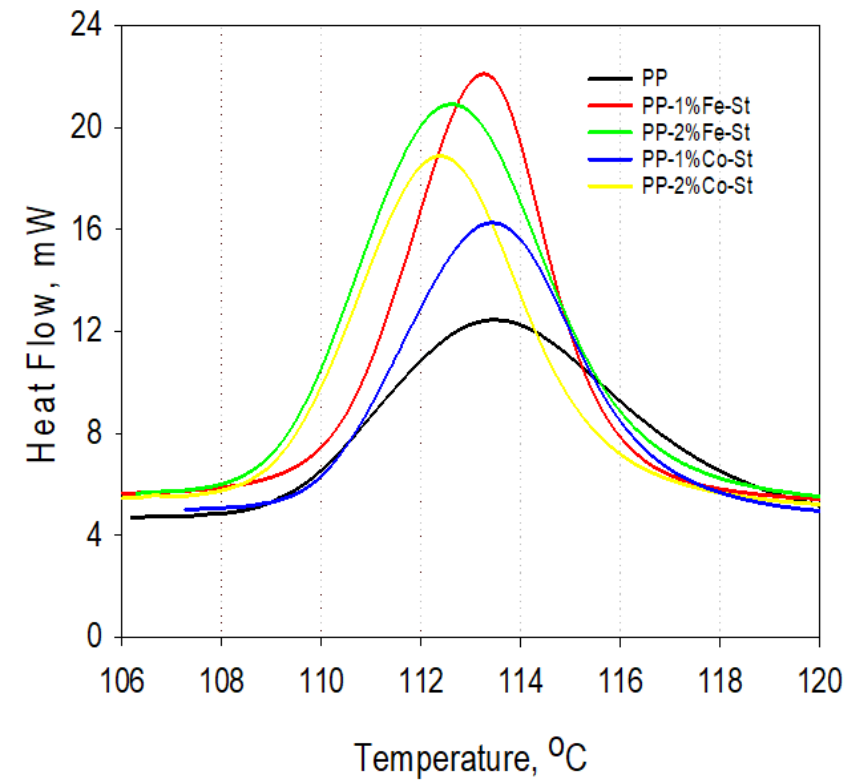
Thermal Analysis unaged PP with and without pro-oxidant additive



Differential Scanning Calorimetry
Melting point of PP and PP with prooxidant



Crystallization Points
PP and PP-Pro-oxidants

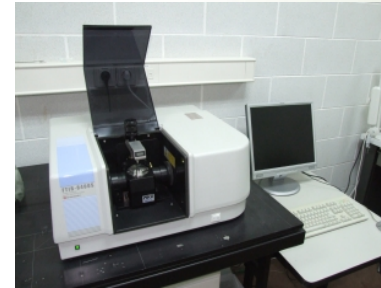
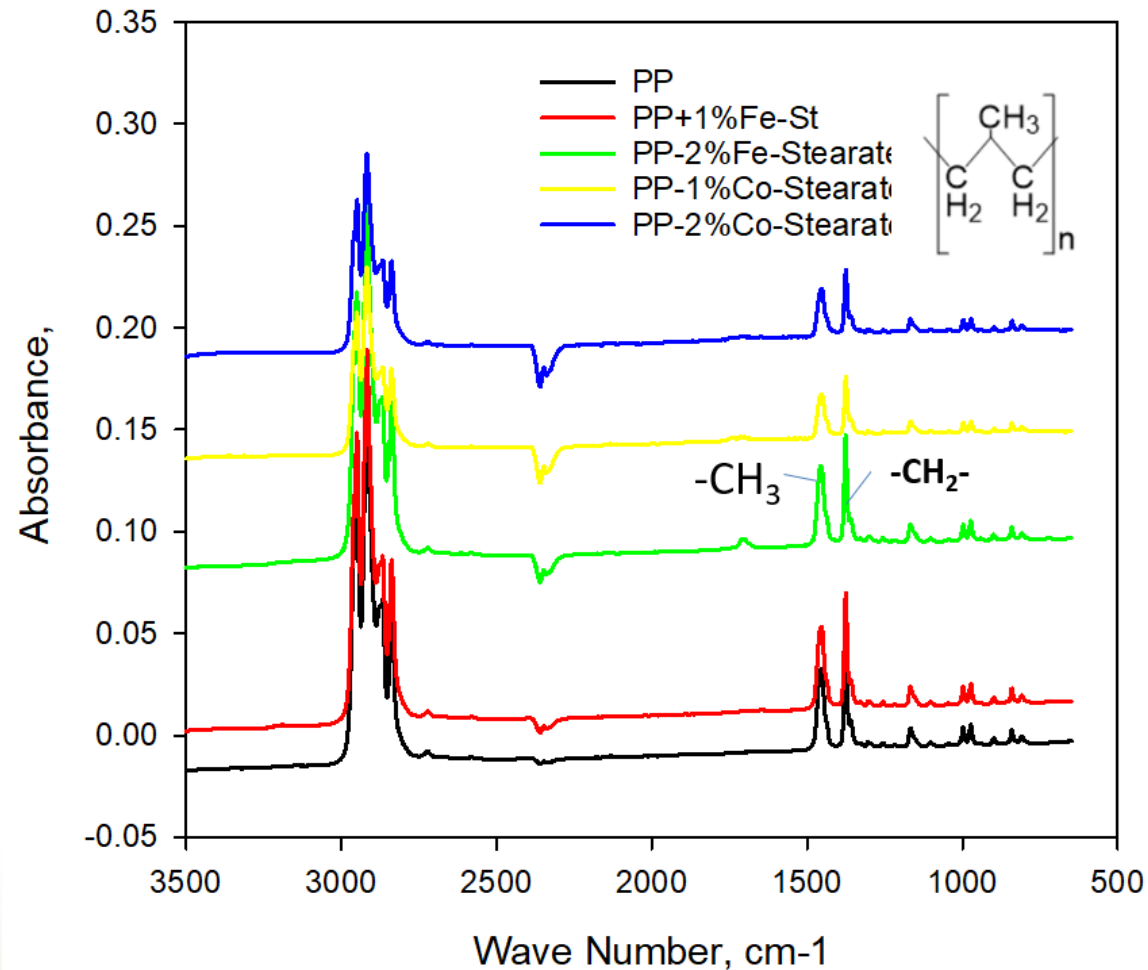


- **Similar melting 160°C. /crystallization temperatures 110 and 114°C**

Fourier-transform infrared spectroscopy analysis surface chemistry



FTIR of PP and PP-Prooxidant additives



No difference in FTIR spectra of PP and PP with prooxidant filler → similar chemical properties

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



Aging time

PP

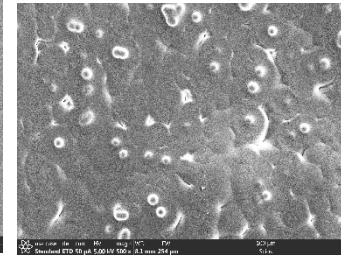
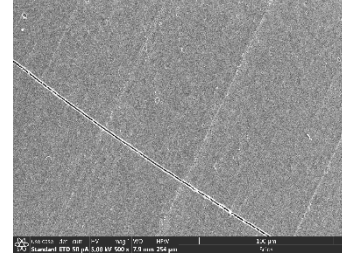
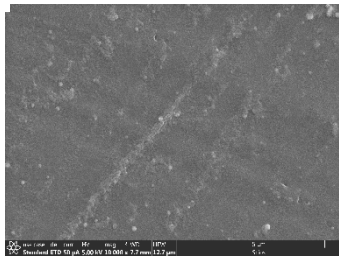
PP-1%Co-St

PP-2%Fe-St

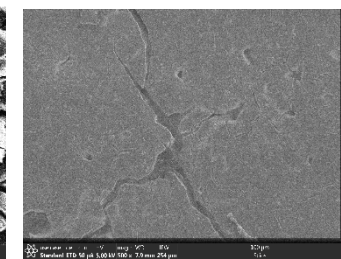
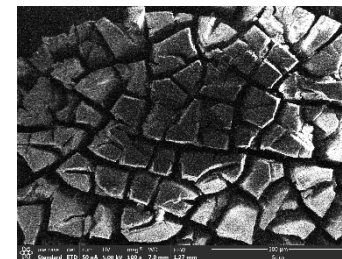
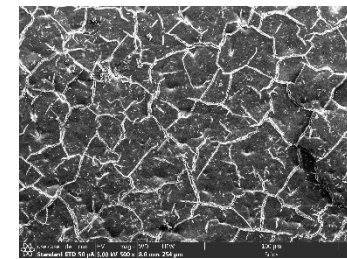
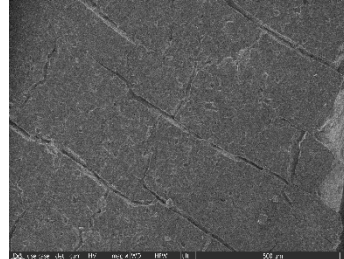
PP-1%Co-St

PP-2%Co-St

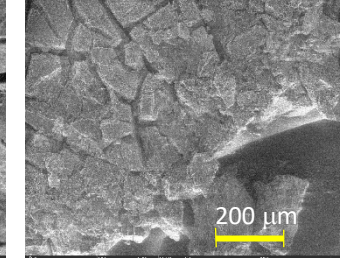
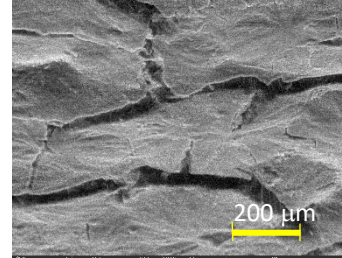
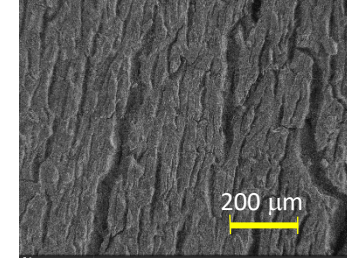
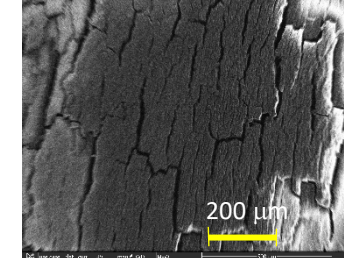
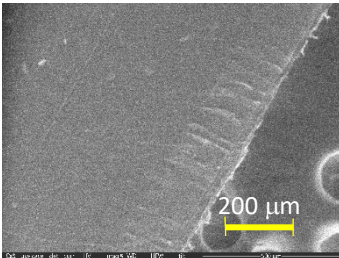
0 h



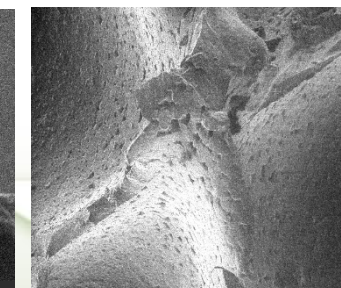
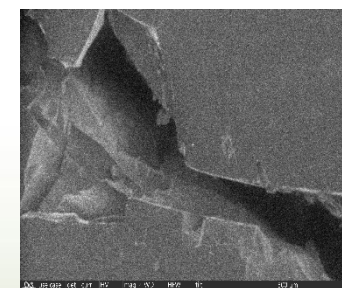
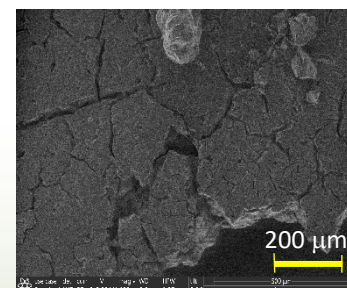
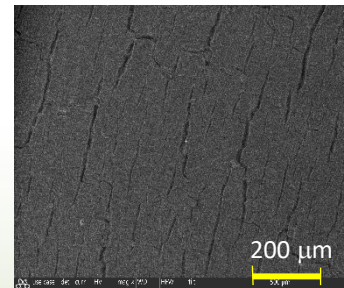
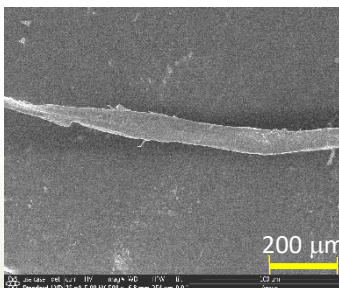
318 h



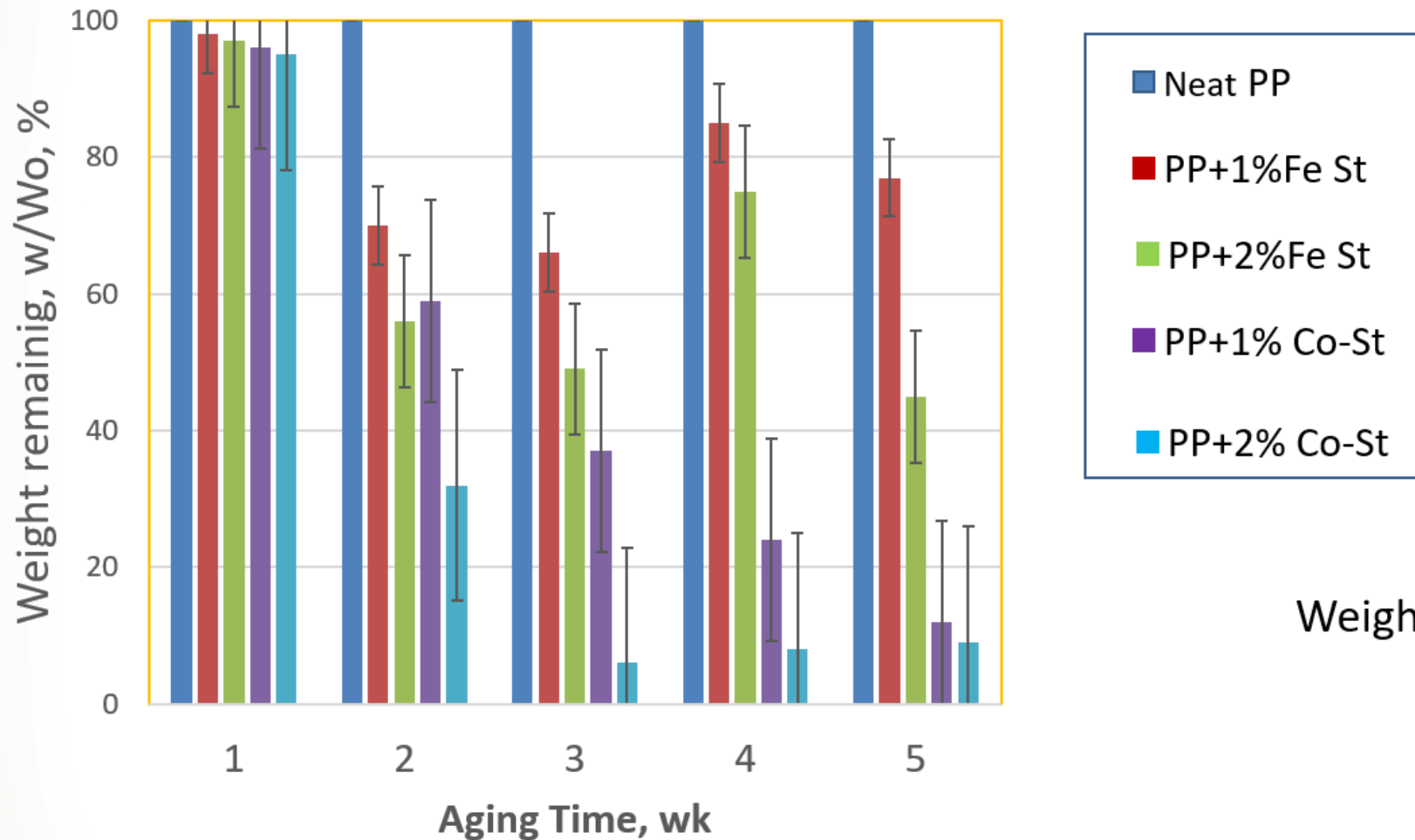
400 h



500 h



Accelerated aging of PP with pro-oxidant

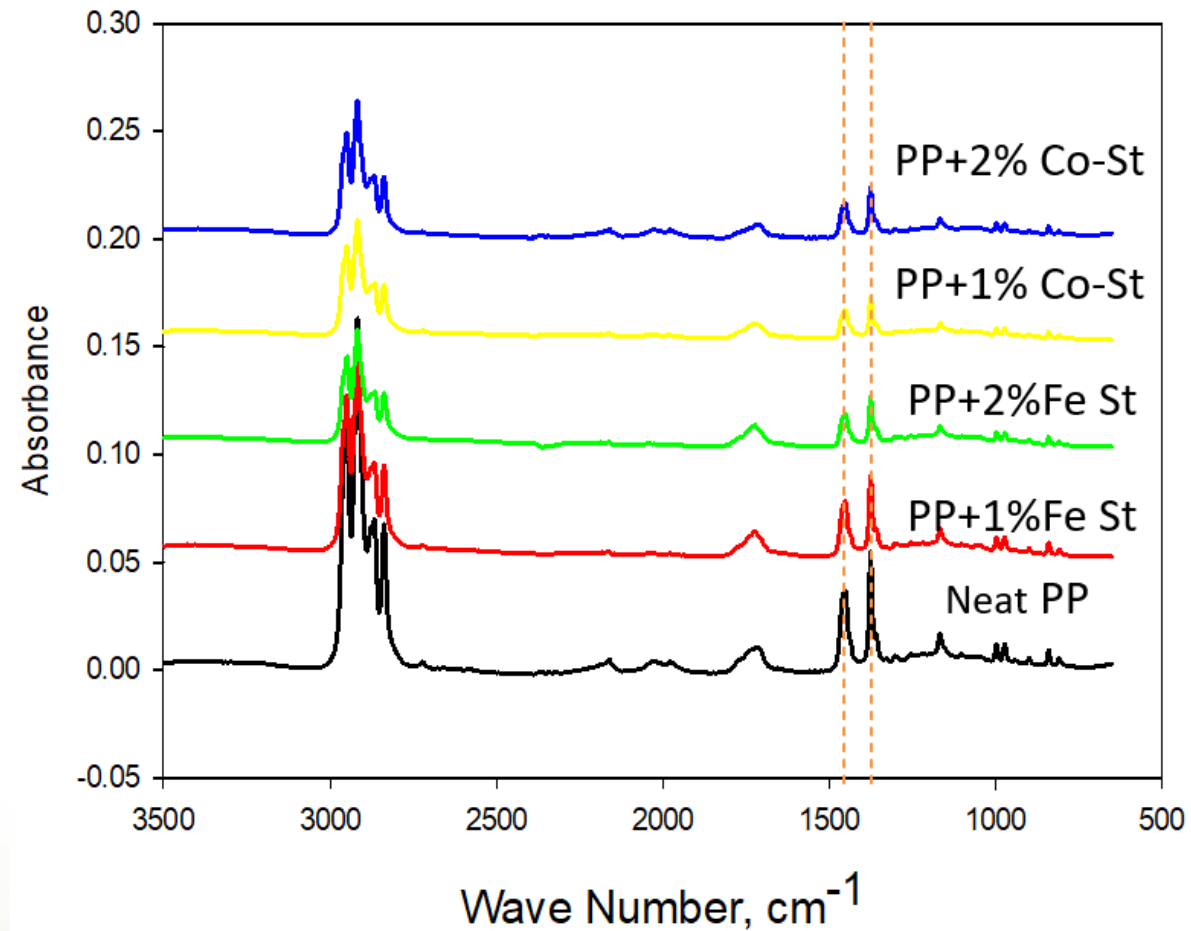


Weight loss depends

FT IR of aged polymers



Weathering time, 318 h

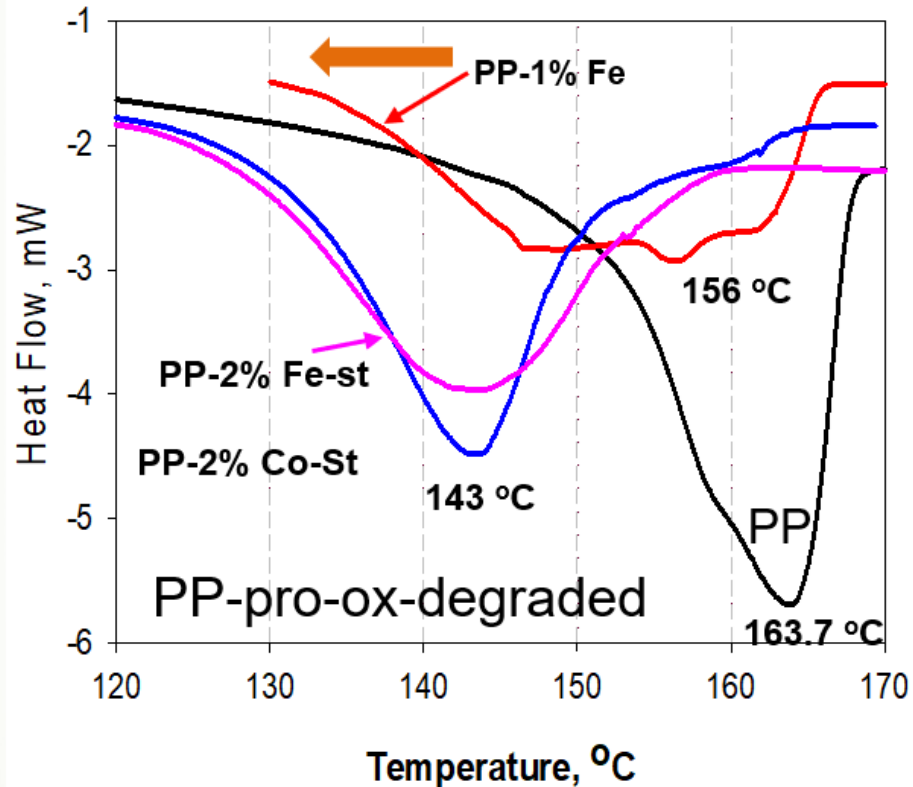


Differential scanning calorimetry



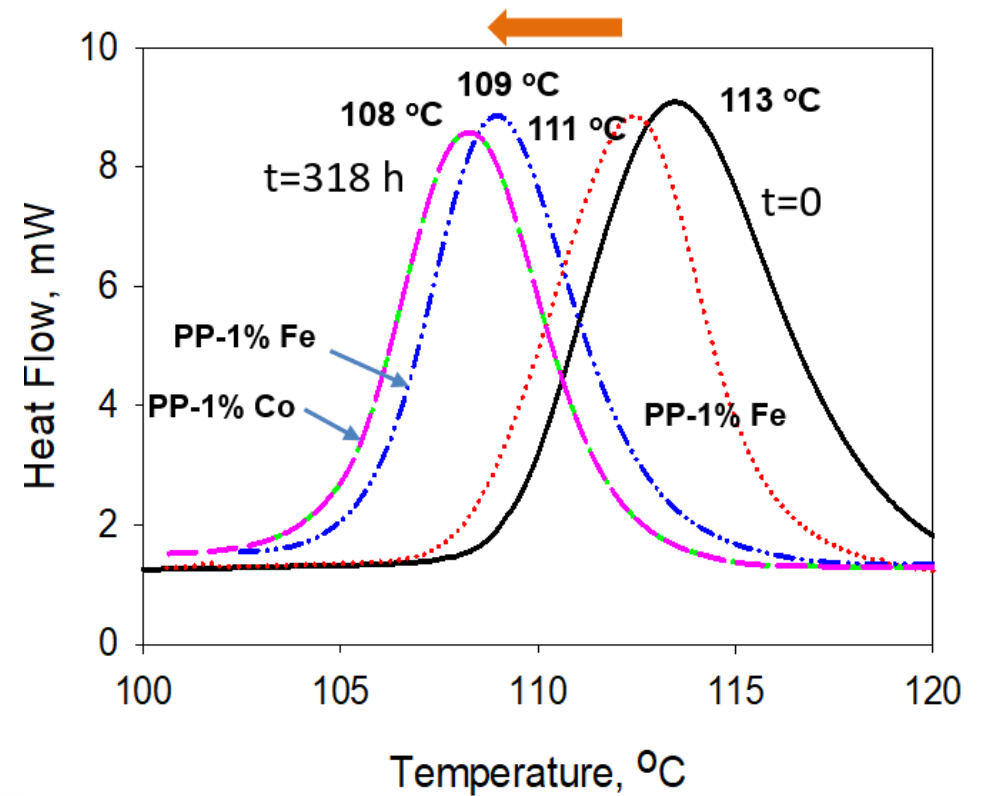
Melting point decreases after 318 h aging

change Tm after 318 h

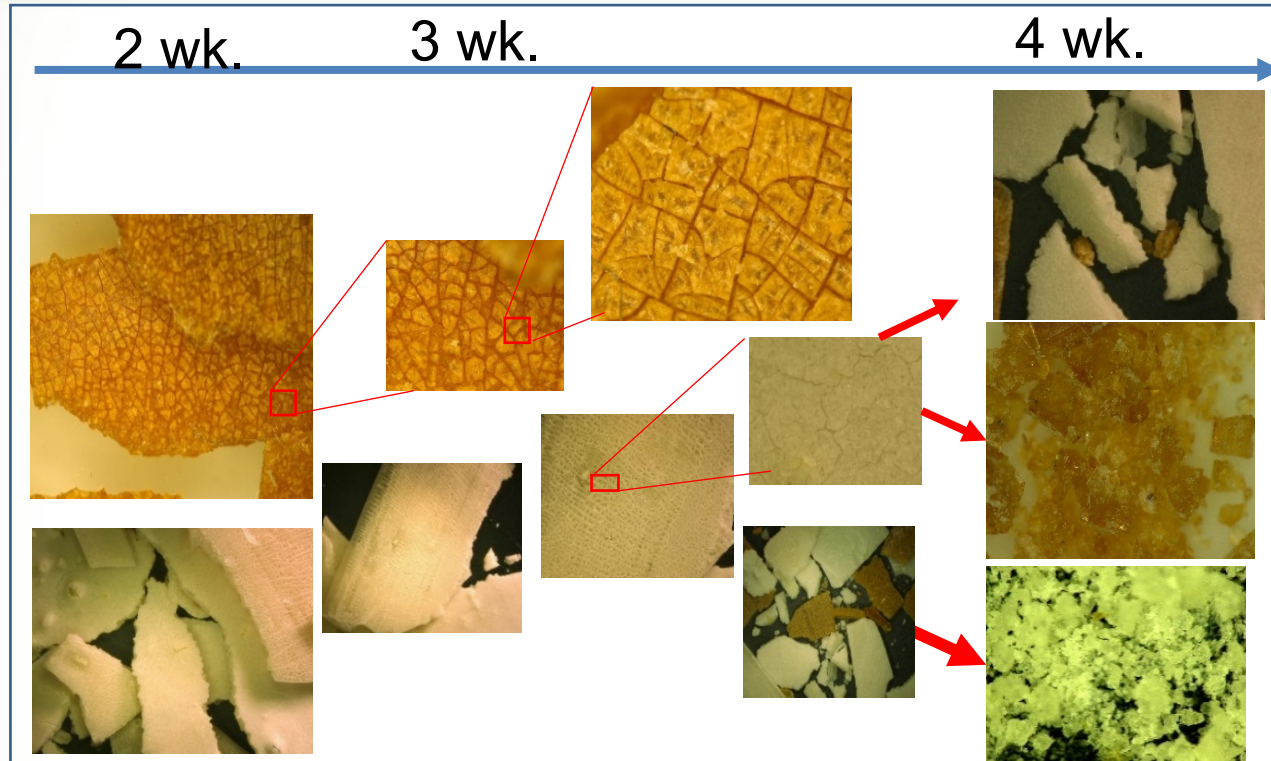


Crystallization Temp. drops after 318 h aging

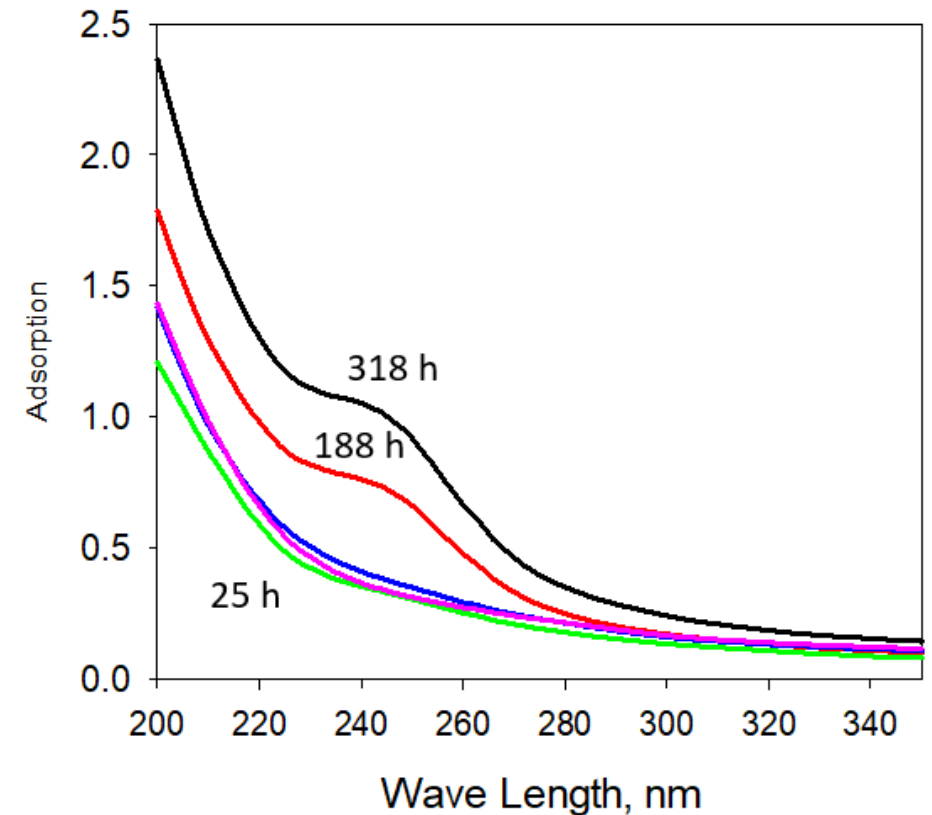
Changes in Crystallization Temperatures with ProOxidant filled PP



PP degradation and wash water analysis

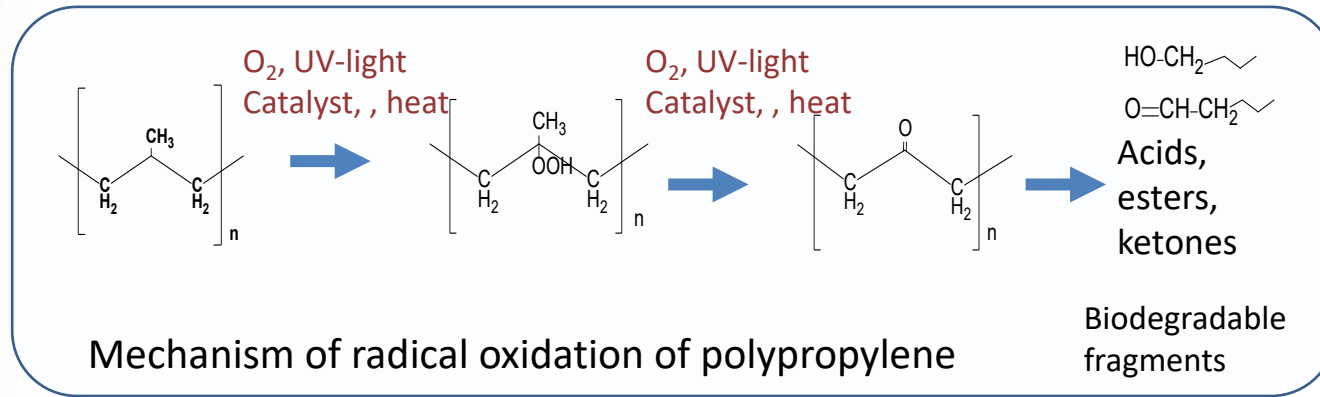


Digital images showing stages of PP degradation

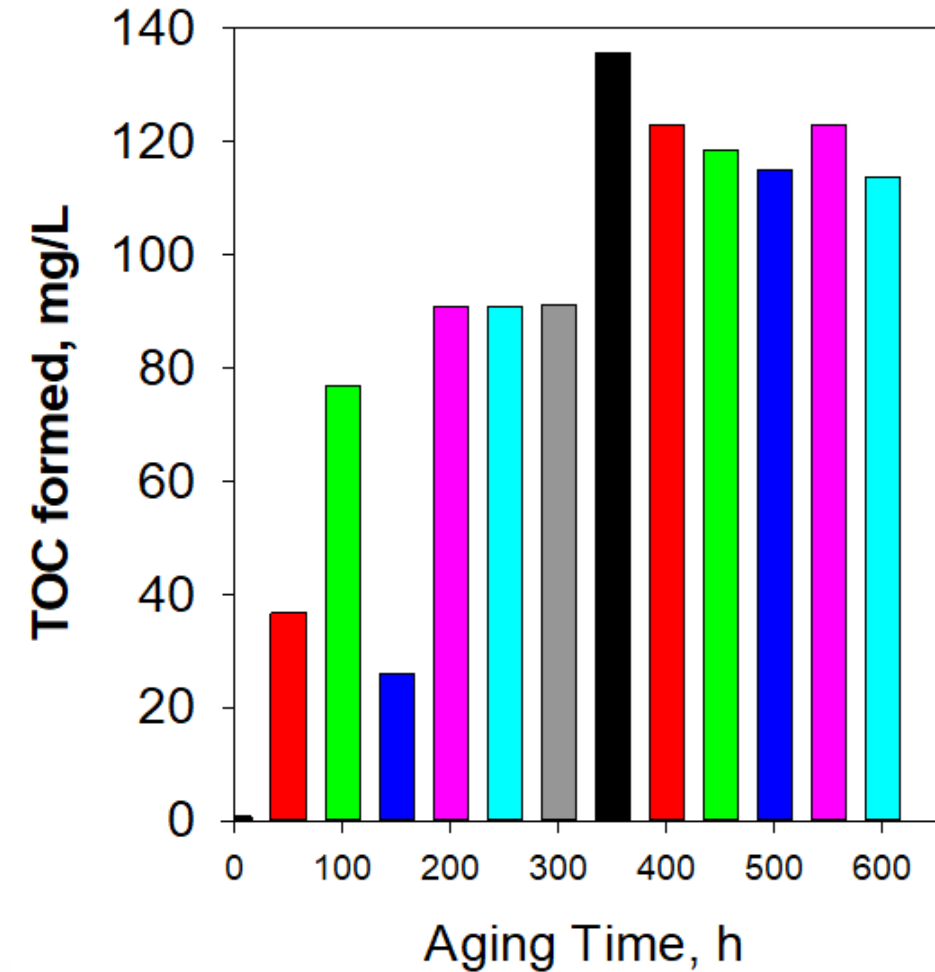


Wash-water analysis show absorbance at 254 nm with aging time indicate pp degradation products that are water soluble, could be biodegradable

Proposed environmental degradation mechanism



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

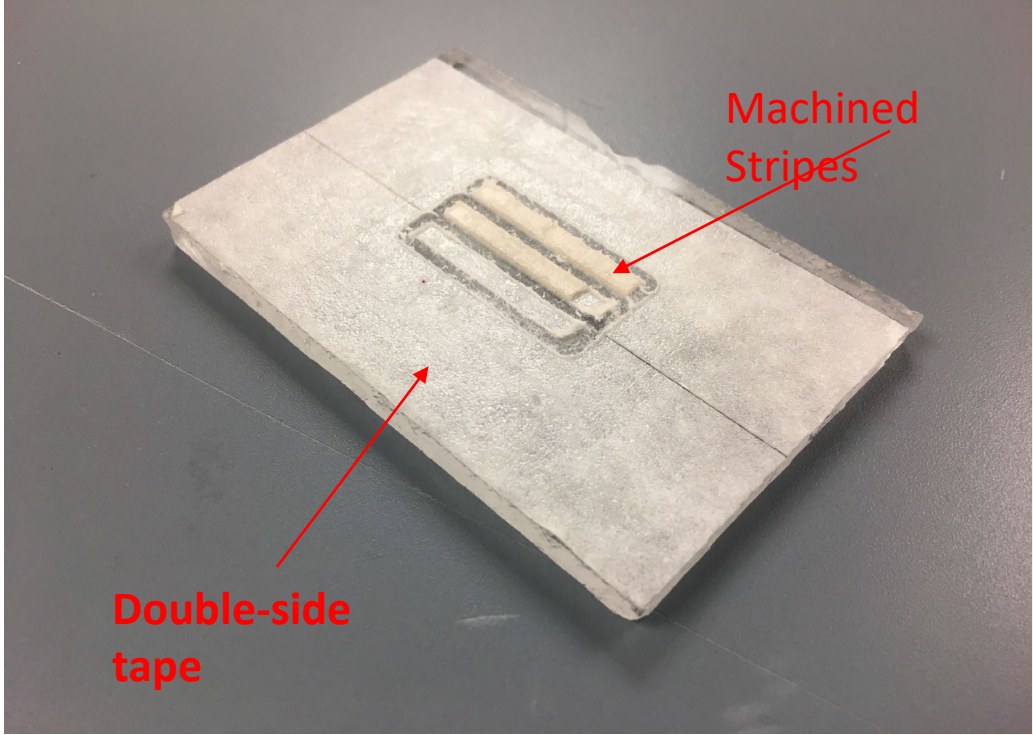


Sample Processing

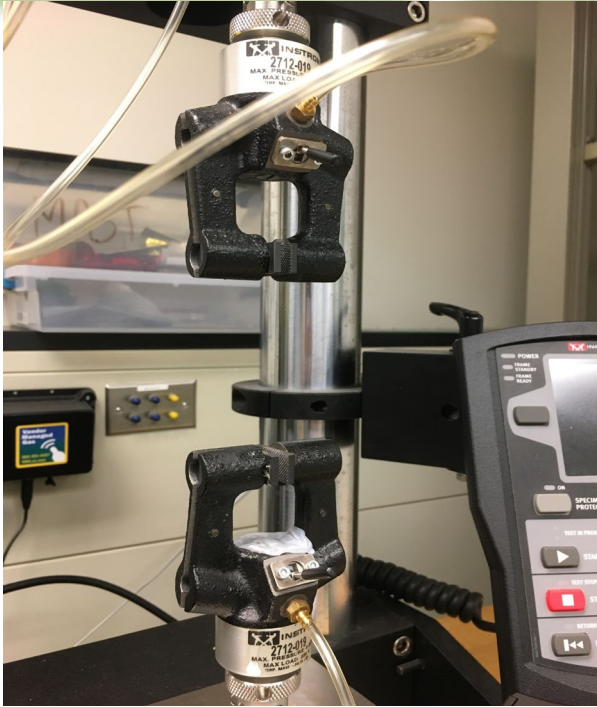
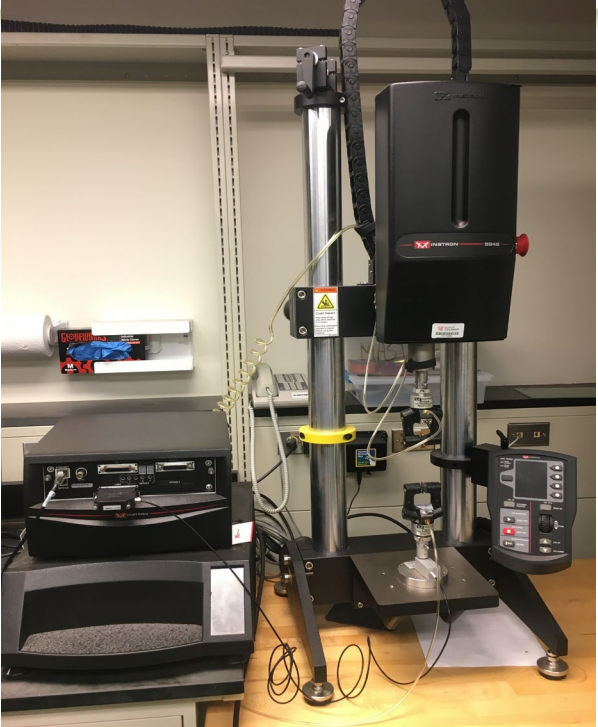
- Ionic bond + laser machining
glue bonding is good
sample size programable
laser burns the polymer
- Micro-milling machining
taped on a stage
sample size programable
mechanical machining



Micro-milling of LDPE

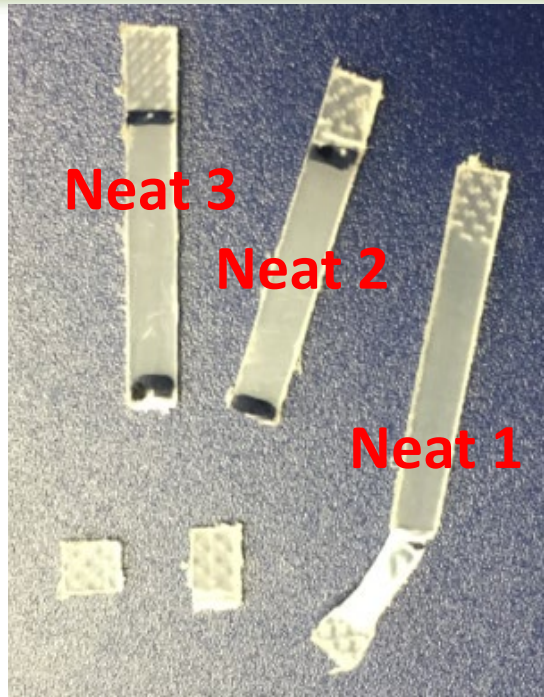


Mechanical Testing of PP

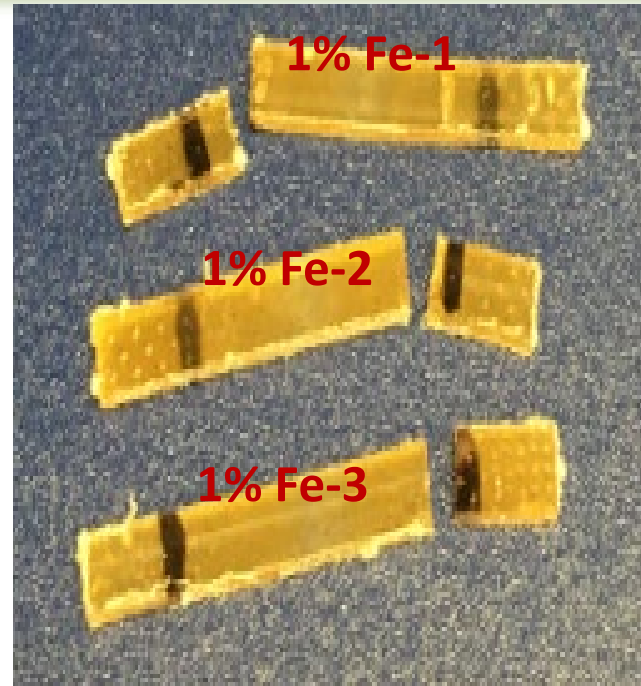


Sample ID	Size (mm)	Strain Rate (mm/min)
Neat 1	4x1x25	0.5
Neat 2	4x1x25	1
Neat 3	4x1x25	1
1% Fe-1	4x1x25	1
1% Fe-2	4x1x25	1
1% Fe-3	4x1x25	1

Tensile test strip samples



Neat PP samples strips



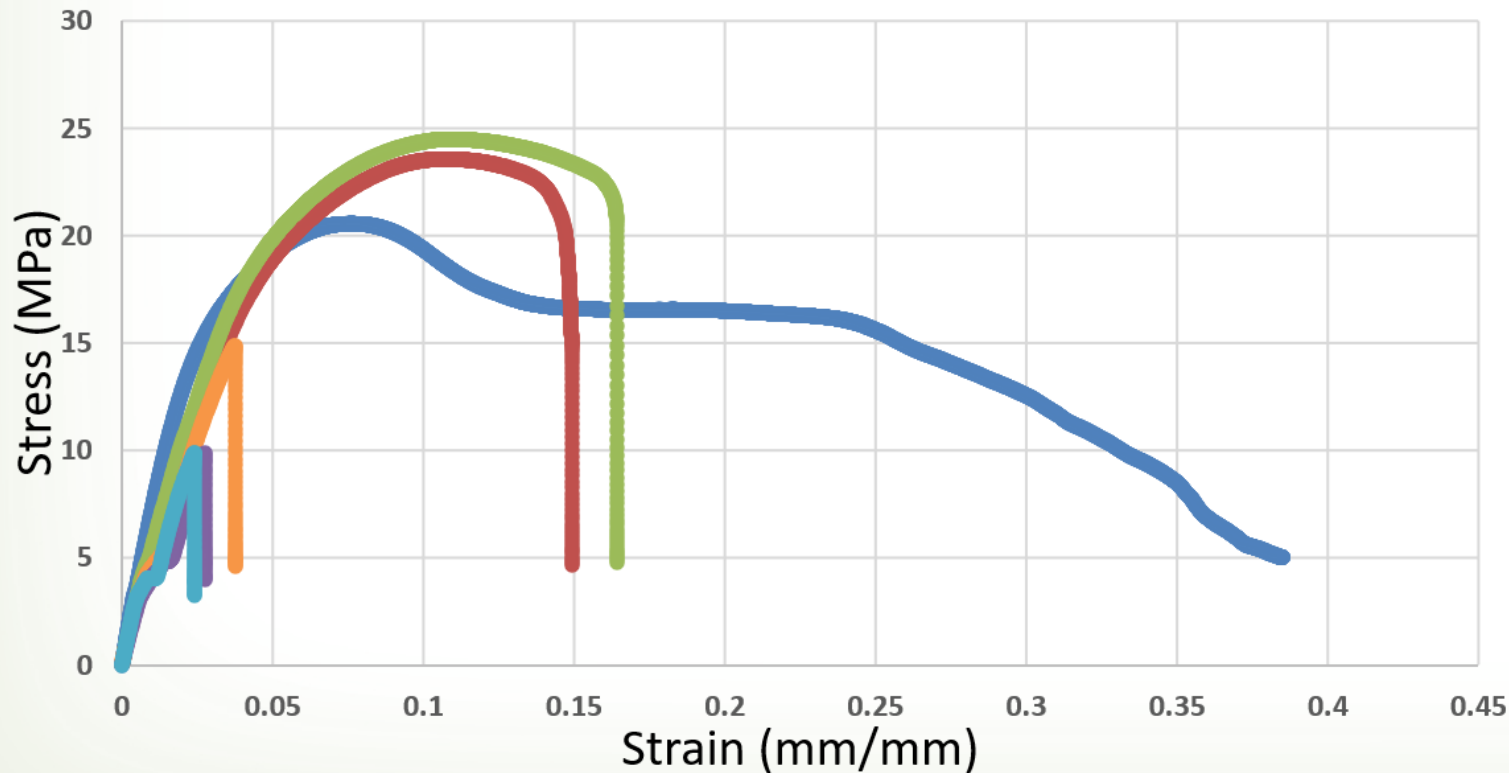
PP with Fe-stearate
additives samples strips

Tensile strength test result



Strain-Stress Curve of LDPE

● Neat 1 ● Neat 2 ● Neat 3 ● 1%Fe 1 ● 1%Fe 2 ● 1%Fe 3



- 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 depolymerization 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



The views expressed in this presentation are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency. Any mention of trade names or external references does not indicate endorsement by the EPA.

Thank you



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Thank you

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