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Introduction to Thermoplastic Materials

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January 21, 2021

Introduction to Thermoplastics
The Madison Group
608-231-1907

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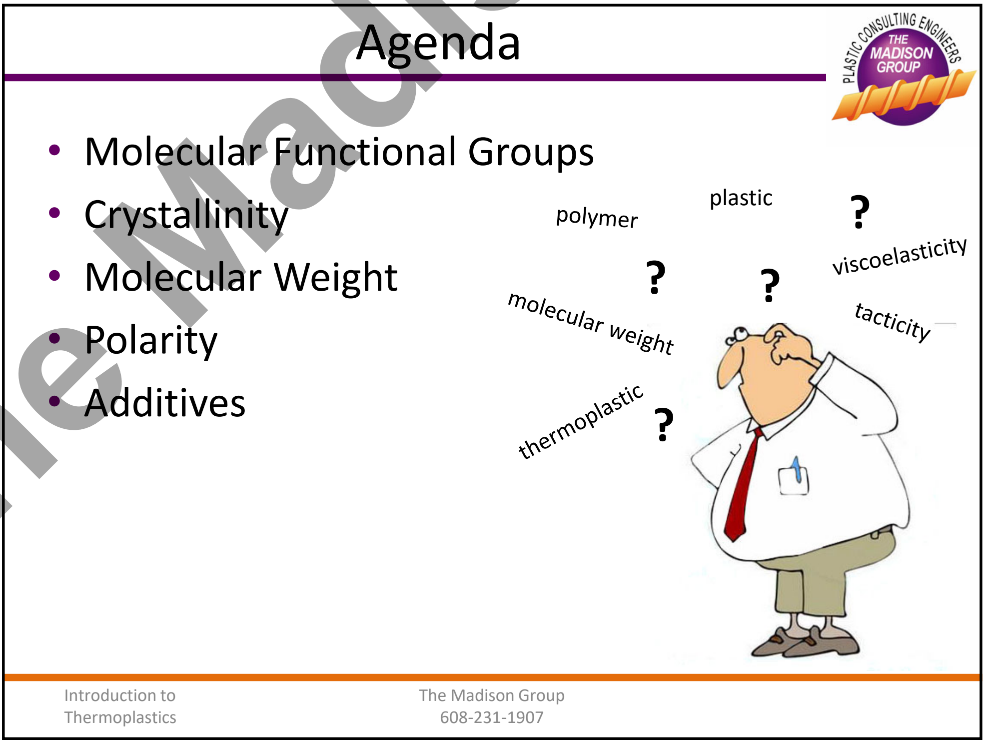

Agenda

- Molecular Functional Groups
- Crystallinity
- Molecular Weight
- Polarity
- Additives

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Plastic Characteristics

Molecular Structure

- Average Molecular Weight
- Molecular Weight Distribution
- Branching
- Tacticity
- Crystallinity
  - Amorphous
  - Semi-crystalline
- Crosslinking
  - Thermoplastic
  - Thermoset

Material Composition

- Base Polymer
  - Functional Groups
  - Homopolymer / Copolymer
  - Blends / Alloys
- Additives
  - Modifiers
  - Anti-degradants
  - Colorants
  - Fillers

Plastic Characteristics

Molecular Structure

Material Composition

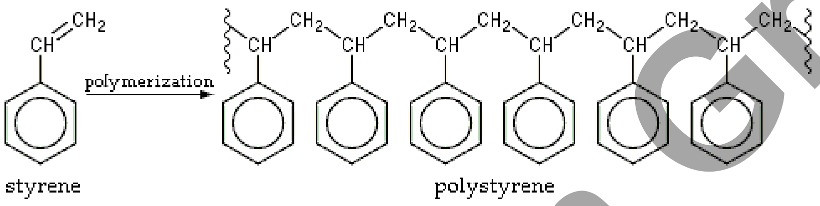
- Base Polymer
  - Functional Groups

Polymerization

Addition Polymerization

- Formation of polymers from monomers containing a **C=C** bond through an addition reaction.

Exothermic Reaction

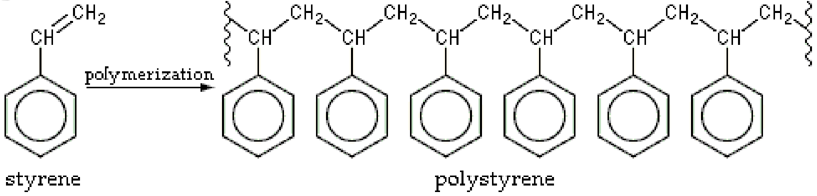


Polymerization

Addition Polymerization

- Many monomers bond together via rearrangement without the loss of any atom or molecule.

Exothermic Reaction

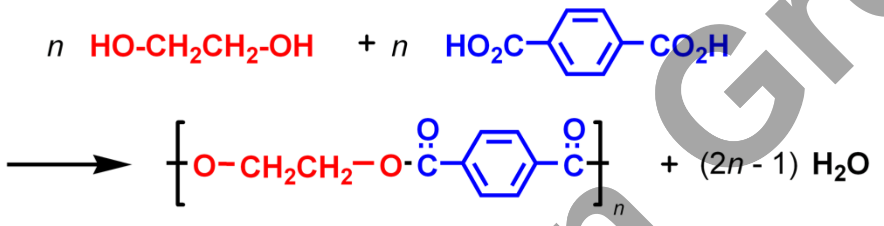


Polymerization

Condensation Polymerization

- Condensation polymers are formed by the reaction of molecules with **two functional groups** and produces water as a by-product.

Endothermic Reaction

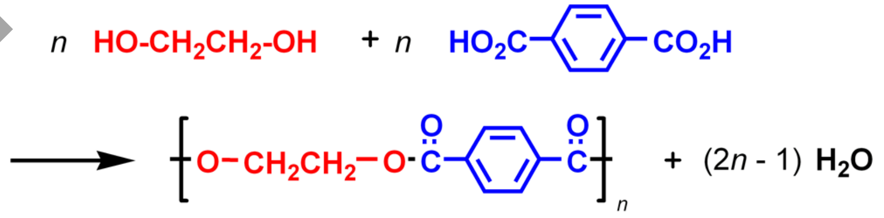


Polymerization

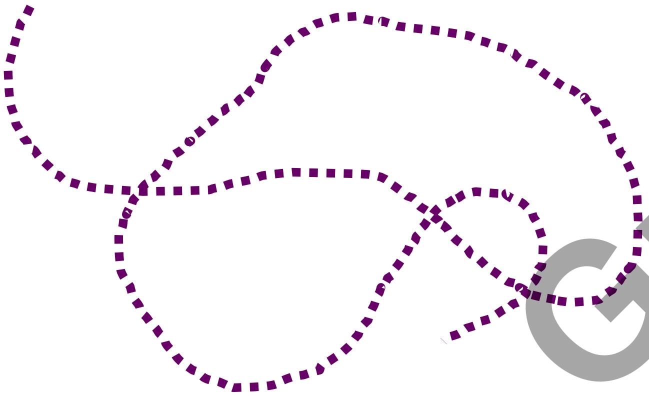
Condensation Polymerization

- Produced form monomers that contain at least two functional groups – or the same functional group twice.

Endothermic Reaction



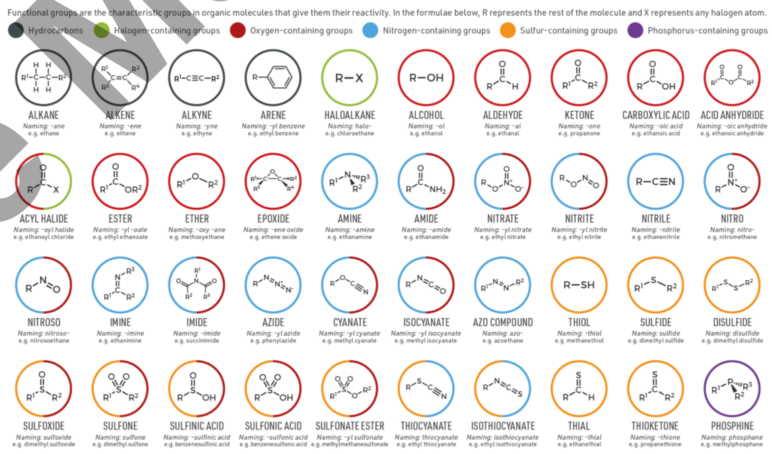
Polymerization

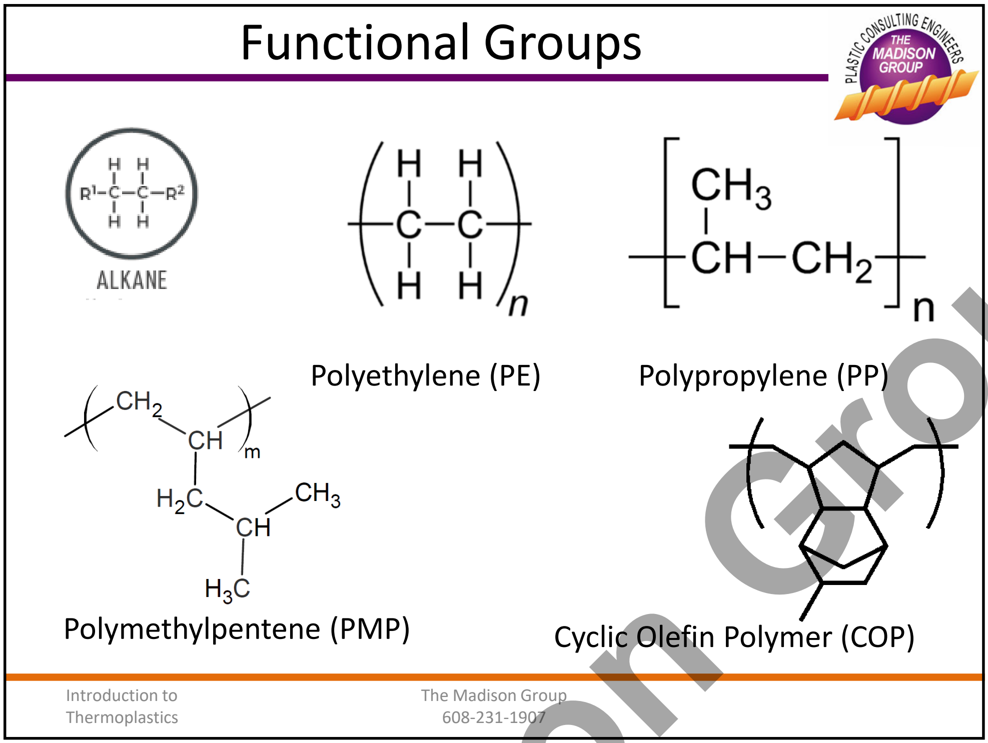


Polymer chain made up of repeating units

Functional Groups

By using different starting materials and processing techniques, polymers having different molecular structures can be produced.





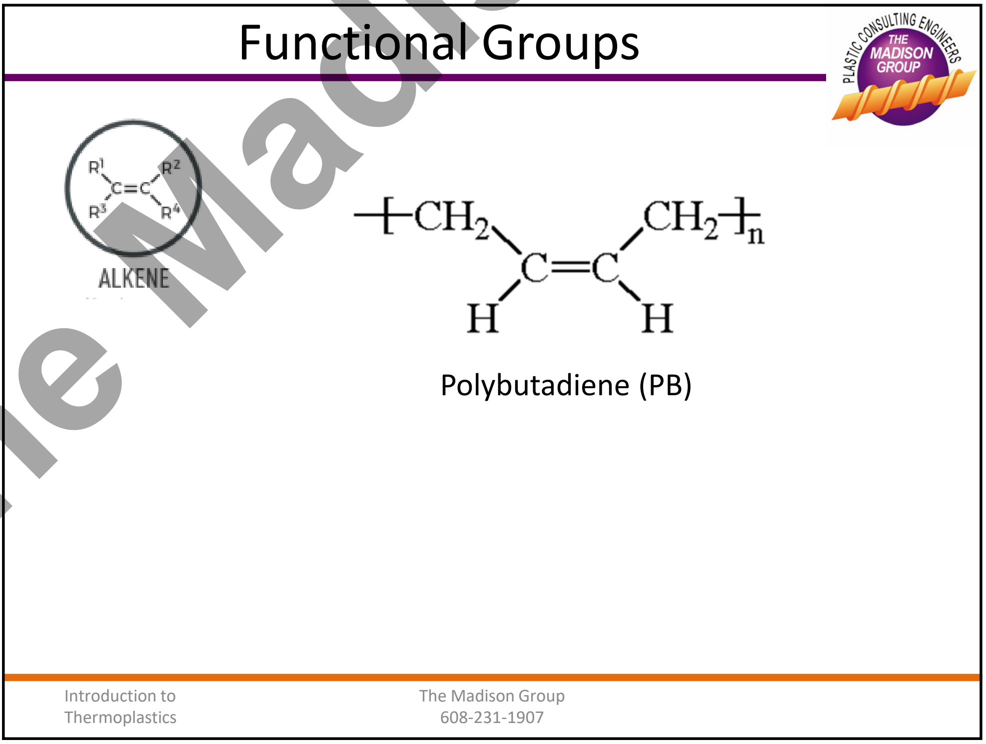
Functional Groups

Polyethylene (PE)

Polypropylene (PP)

Polymethylpentene (PMP)

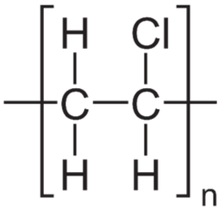
Cyclic Olefin Polymer (COP)



Functional Groups

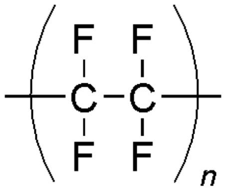
Polybutadiene (PB)

Functional Groups



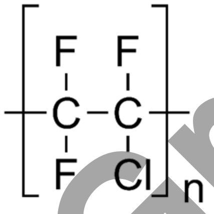
$$\left[\mathrm{CH_2{-}CHCl}\right]_n$$

Poly(vinyl chloride) (PVC)



$$\left(\mathrm{CF_2{-}CF_2}\right)_n$$

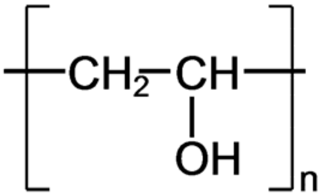
Polytetrafluoroethylene (PTFE)



$$\left[\mathrm{CF_2{-}CFCl}\right]_n$$

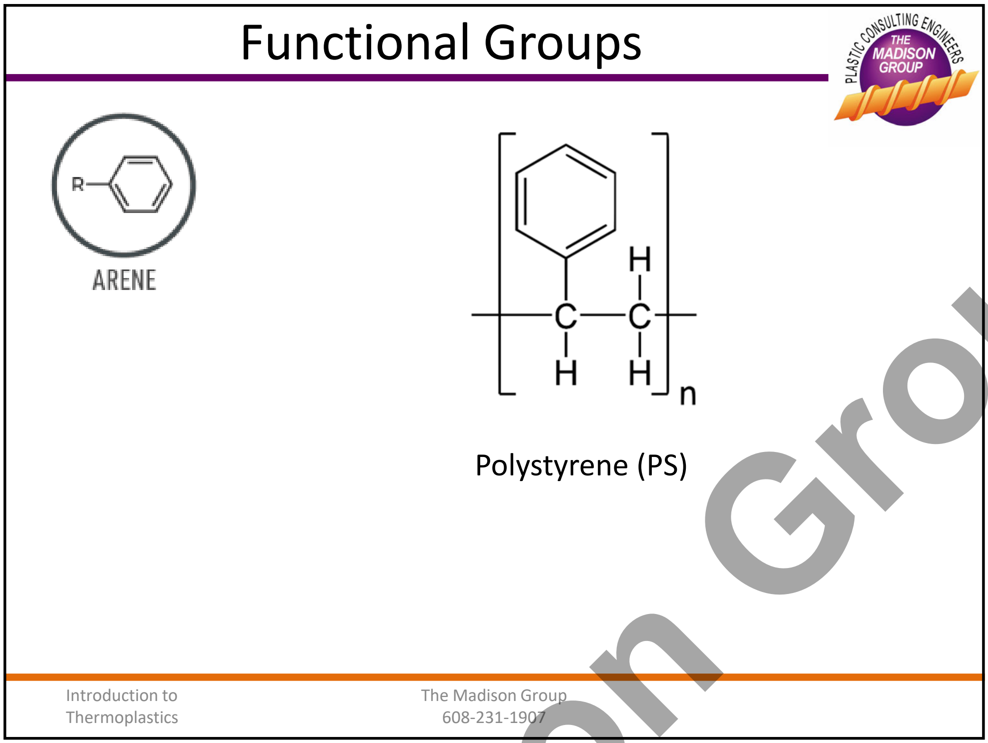
Polychlorotrifluoroethylene (PTFE)

Functional Groups



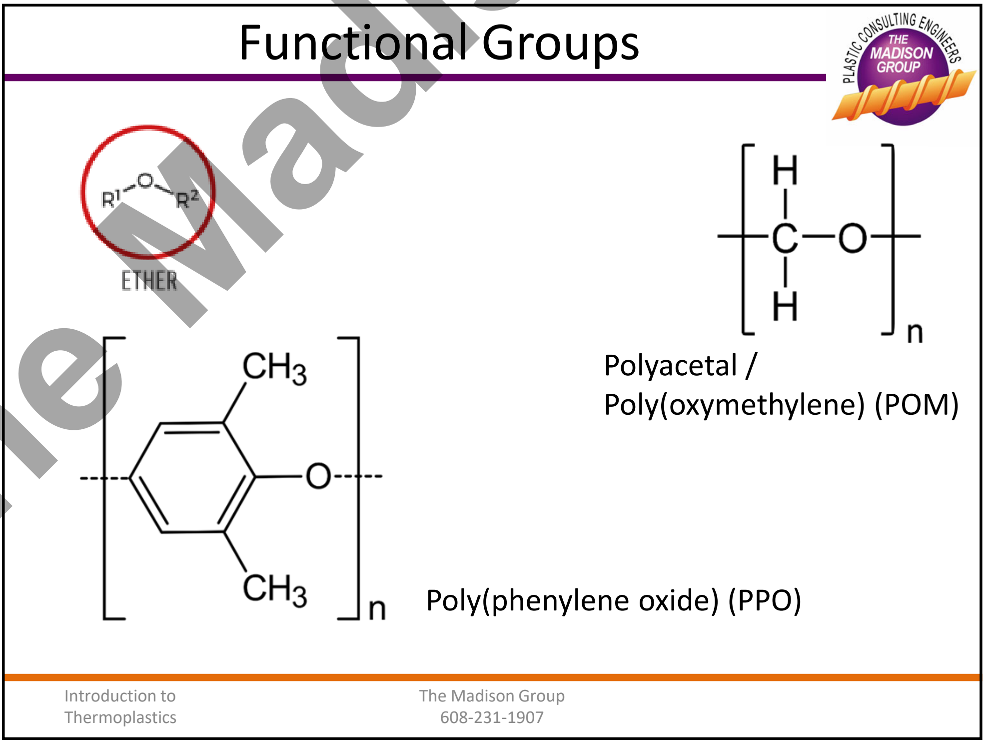
$$\left[\mathrm{CH_2{-}CH(OH)}\right]_n$$

Poly(vinyl alcohol) (PVOH)



Functional Groups

Polystyrene (PS)

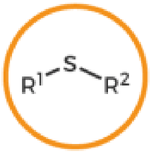


Functional Groups

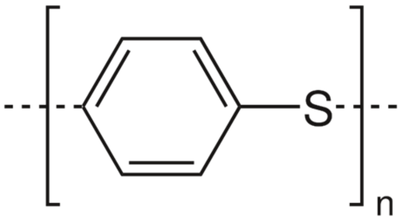
Polyacetal /
Poly(oxymethylene) (POM)

Poly(phenylene oxide) (PPO)

Functional Groups

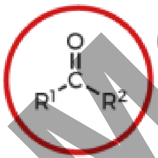


SULFIDE

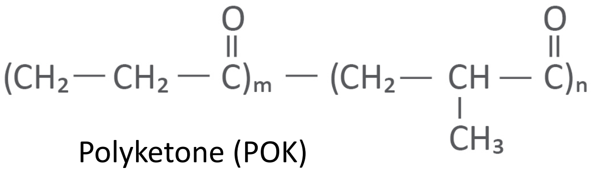


Poly(phenylene sulfide) (PPS)

Functional Groups

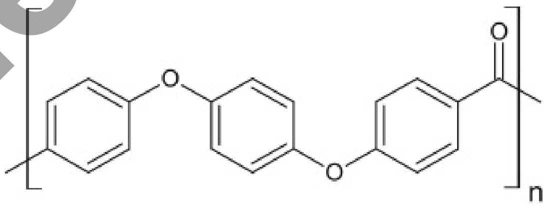


KETONE



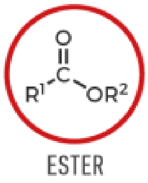
$$(CH_2-CH_2-\overset{O}{\overset{\|}{C}})_m-(CH_2-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}})_n$$

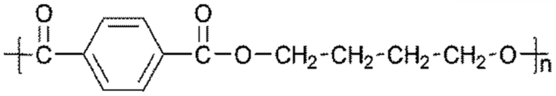
Polyketone (POK)



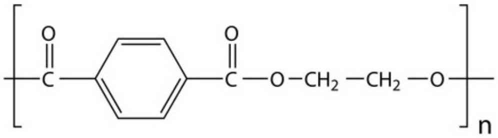
Polyetheretherketone (PEEK)

Functional Groups



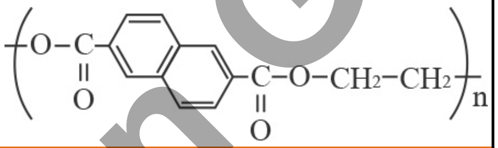


Poly(butylene terephthalate) (PBT)

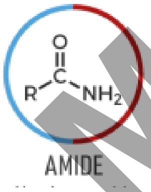


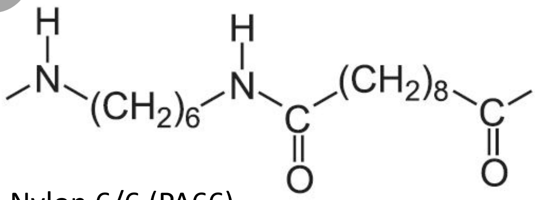
Poly(ethylene terephthalate) (PET)

Poly(ethylene naphthalate) (PEN)

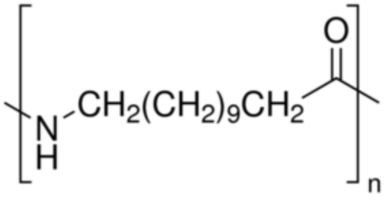


Functional Groups



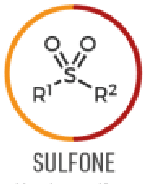


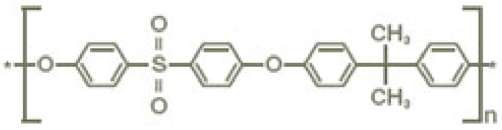
Nylon 6/6 (PA66)



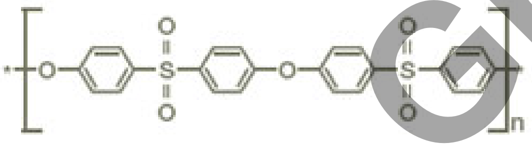
Nylon 12 (PA12)

Functional Groups



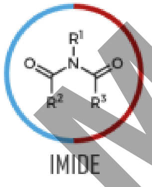


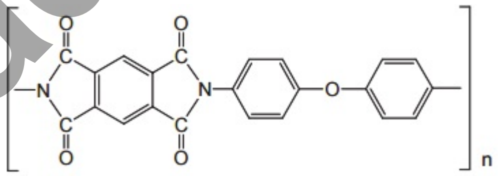
Polysulfone (PSU)



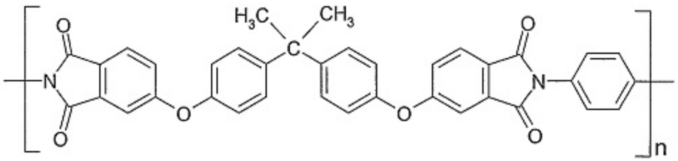
Polyethersulfone (PESU)

Functional Groups





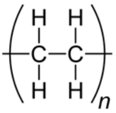
Polyimide (PI)



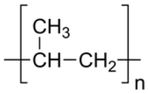
Polyetherimide (PEI)

Functional Groups

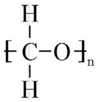
By using different starting materials and processing techniques, polymers having different molecular structures can be produced.



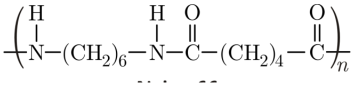
Polyethylene



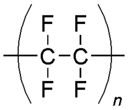
Polypropylene



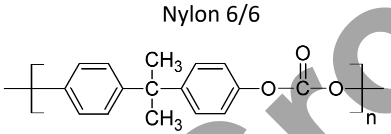
Polyacetal



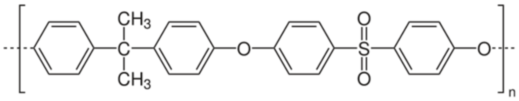
Nylon 6/6



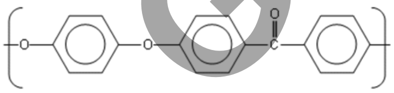
Polytetrafluoroethylene



Polycarbonate



Polysulfone



Poly(etheretherketone)

Plastic Characteristics

Molecular Structure

-
-
- Branching
- Tacticity
- Crystallinity
  - Amorphous
  - Semi-crystalline

Material Composition

- Base Polymer
  - Functional Groups

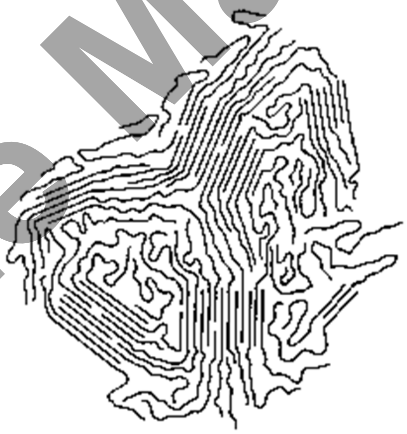
Crystallinity

The crystalline / amorphous structure of a polymer is the result of the molecular architecture –

functional groups, branching, and tacticity.

Crystallinity

<u>Semi-crystalline</u>



<u>Amorphous</u>

Crystallinity

Semi-crystalline

- Polyethylene (PE)
- Polytetrafluoroethylene (PTFE)
- Polypropylene (PP)
- Polyacetal (POM)
- Poly(vinylidene fluoride) (PVDF)
- Poly(ethylene terephthalate) (PET)
- Poly(butylene terephthalate) (PBT)
- Nylon or Polyamde (PA)
- Polyphthalamide (PPA)
- Poly(phenylene sulfide) (PPS)
- Poly(ether ether ketone) (PEEK)

Amorphous

- Poly(vinyl chloride) (PVC)
- Poly(methyl methacrylate) (PMMA)
- Polystyrene (PS)
- Poly(styrene:acrylontrile) (SAN)
- Poly(acrylonitrle:butadiene: styene) (ABS)
- Polycarbonate (PC)
- Poly(phenylene oxide) (PPO)
- Polysulfone (PSU)
- Poly(ether imide) (PEI)

Crystallinity - Amorphous

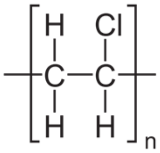
Amorphous polymers have a molecular structure that is exclusively random
Only a glass transition (Tg).

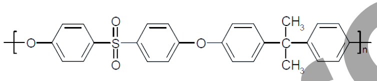
This is the result of the molecular structure – inability of the molecules to form an orderly pattern.

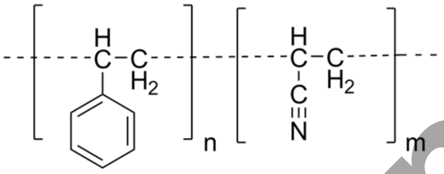
Crystallinity - Amorphous

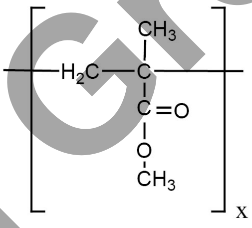
Amorphous polymers have a molecular structure that is exclusively random
Only a glass transition (Tg).

This is the result of the molecular structure – inability of the molecules to form an orderly pattern.

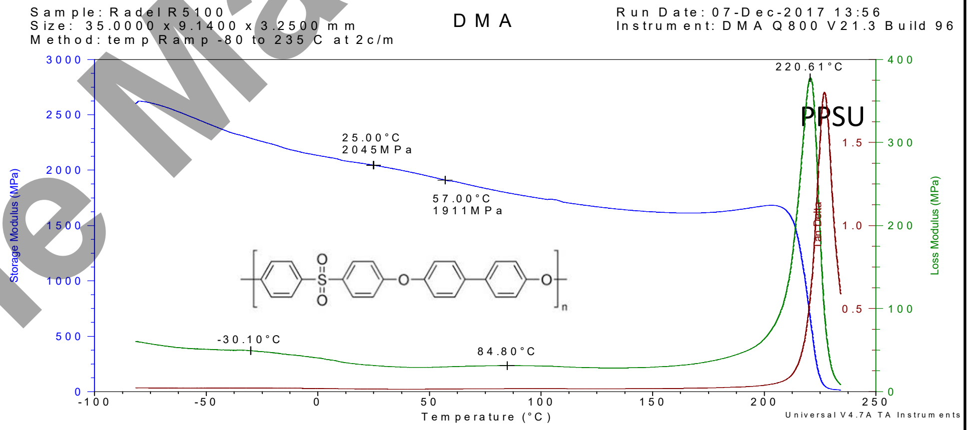






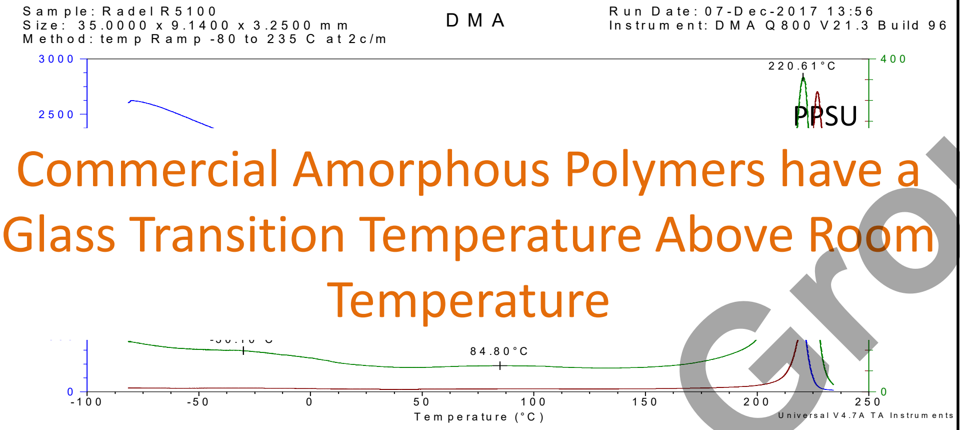


Crystallinity - Amorphous



As an amorphous polymer is heated to its Tg, there is very little change in the mechanical properties of the material.
Once the amorphous polymer reaches the Tg, it begins to gradually soften.

Crystallinity - Amorphous



Commercial Amorphous Polymers have a Glass Transition Temperature Above Room Temperature

As an amorphous polymer is heated to its Tg, there is very little change in the mechanical properties of the material.

Once the amorphous polymer reaches the Tg, it begins to gradually soften.

Crystallinity – Semi Crystalline

Semi-crystalline polymers have amorphous and crystalline regions.
Have both a Tg and a melt temperature (Tm)

This is due to the ability of the molecular morphology to partially form an orderly pattern.

No such thing as a 100% crystalline polymer.

Crystallinity – Semi Crystalline

Ability of a material to form a crystalline structure upon cooling is complex, but is related to:

1) Complexity/rigidity of molecule
Molecules with large benzene rings in its backbone, make them more rigid and less likely to align than Polyethylene

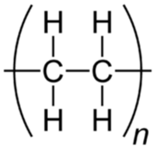
2) Intermolecular forces

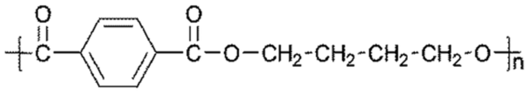
Polymer	Crystalline growth rate	Maximum crystallinity
PE	High	High
PA 66		
PA 6		
PP		
PET		
PS		
PC	Low	Low

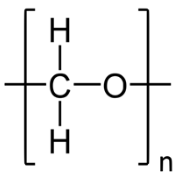
Crystallinity – Semi Crystalline

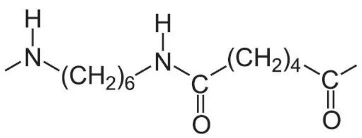
Semi-crystalline polymers have amorphous and crystalline regions.
Have both a Tg and a melt temperature (Tm)

This is due to the ability of the molecular morphology to partially form an orderly pattern.

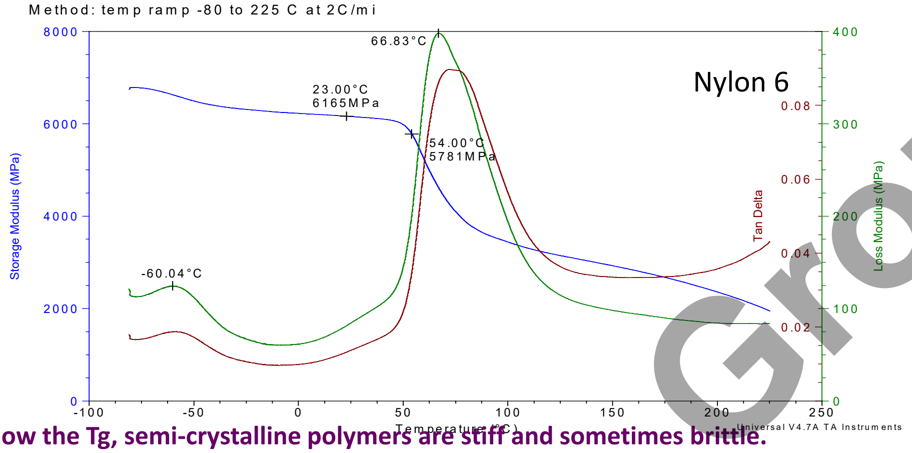








Crystallinity – Semi Crystalline



Below the Tg, semi-crystalline polymers are stiff and sometimes brittle.
Above the Tg but below the Tm, act as a soft, leathery solid, but do not flow.
Above the Tm, the crystalline regions melt and the polymer can flow.

Crystallinity – Semi Crystalline

Sample: Dry as Molded - No Knit Line
Size: 35.0000 x 12.4800 x 3.0500 mm
Method: temp ramp -80 to 225 C at 2C/mi
DMA
Run Date: 09-Jan-2018 11:29
Instrument: DMA Q800 V21.3 Build 96

Semi-Crystalline Thermoplastics

With Tg below ambient, like PE, POM, and PP
Behave more soft and leathery due to amorphous regions being flexible

With Tg above ambient, like PA 66, PET, and PEEK
Behave more stiff and rigid at room temperature, but will soften above the Tg

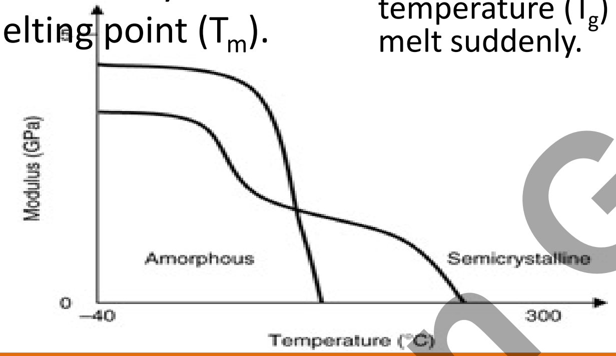
Crystallinity

Semi-crystalline

- Regular order or pattern of molecular arrangement. They have a sharp melting point (T_m).

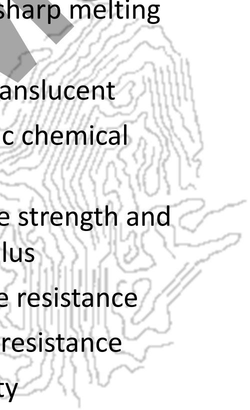
Amorphous

- Randomly arranged molecular chains with no long-term order. They soften at a glass transition temperature (T_g) rather than melt suddenly.



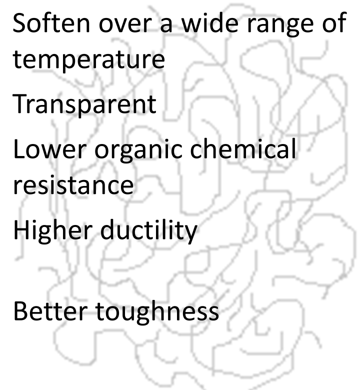
Crystallinity

Semi-crystalline



- Distinct and sharp melting point
- Opaque or translucent
- Better organic chemical resistance
- Higher tensile strength and tensile modulus
- Better fatigue resistance
- Better creep resistance
- Higher density
- Higher mold shrinkage

Amorphous



- Soften over a wide range of temperature
- Transparent
- Lower organic chemical resistance
- Higher ductility
- Better toughness
- Lower density
- Lower mold shrinkage

Plastic Characteristics

Molecular Structure

-
-
- Branching
- Tacticity
- Crystallinity
  - Amorphous
  - Semi-crystalline
- Polarity

Material Composition

- Base Polymer
  - Functional Groups

Polarity

Why does Nylon Absorb Water?

Why does Polyethylene Absorb Gasoline?

Polar likes Polar

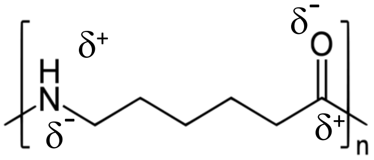
Non-polar likes Non-polar

Polarity

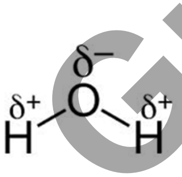
Polarity – Functionality of the Groups

Intermolecular Bonding

Nylon and Water



Nylon 6

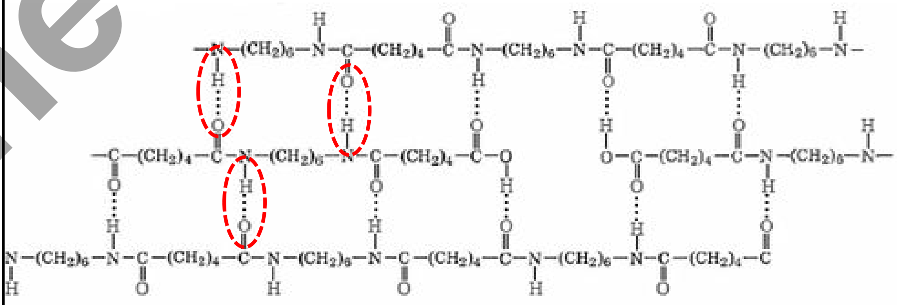


Water

Polarity

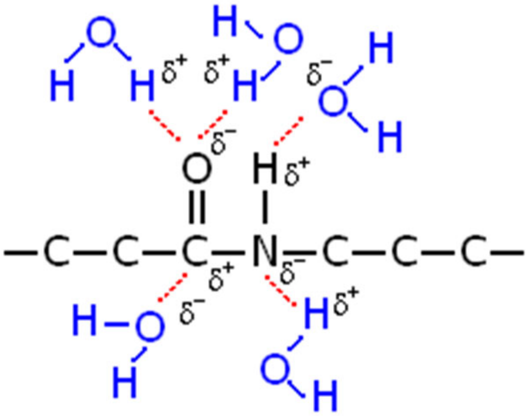
Nylon and Water

Applied stresses – both internal and external - overcome inter-molecular forces such as, Van der Waals forces, London dispersion forces, hydrogen bonding, and dipole interactions



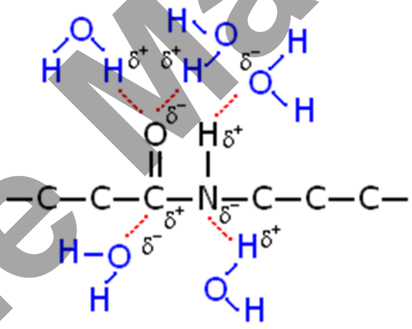
Polarity

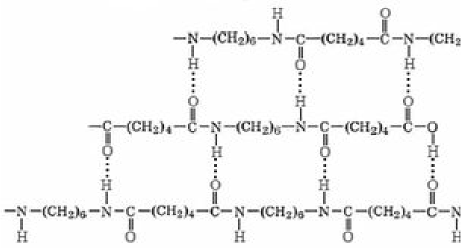
Hydrogen bonding



Ref: IDES Article: **Dry vs. Conditioned Polyamide Nylon Explained**

Polarity

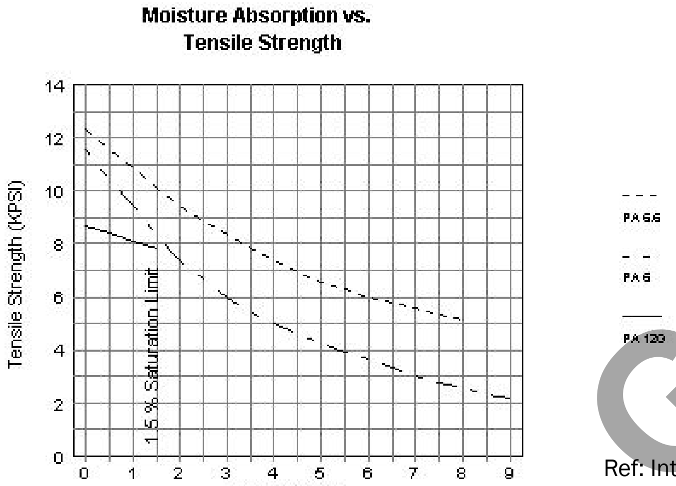




Water interferes with the intermolecular bonding between individual polymer chains – results in changes in physical properties

Polarity

Water absorption reduces tensile strength in nylon resins



Ref: Intech Power: Effects of Moisture Absorption

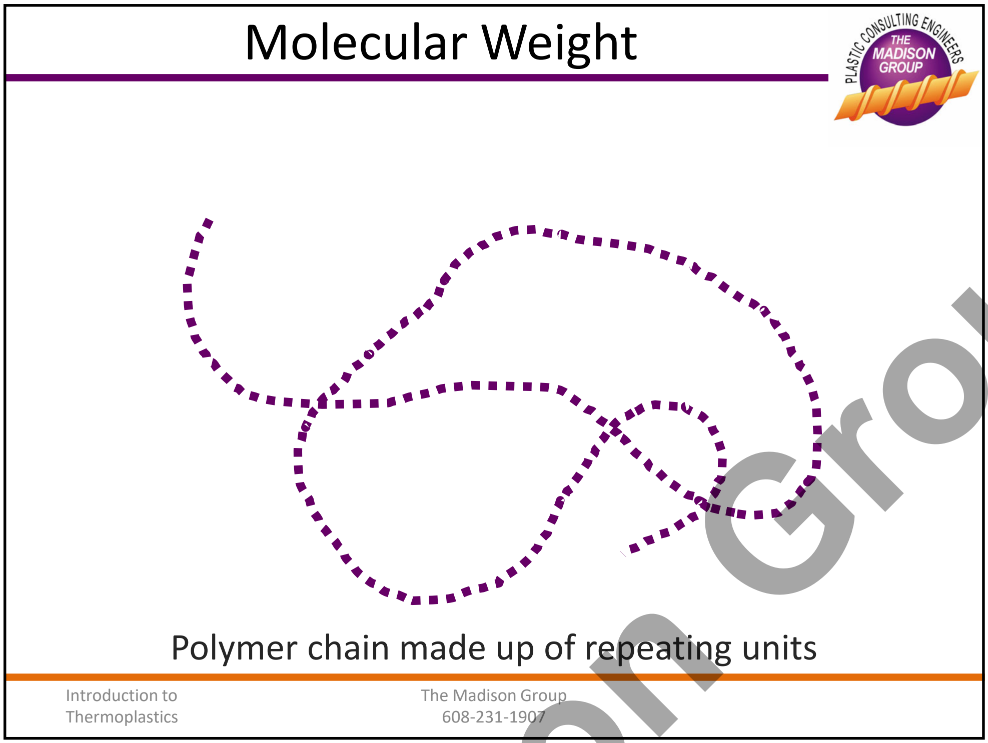
Plastic Characteristics

Molecular Structure

- Average Molecular Weight
- Molecular Weight Distribution
- Branching
- Tacticity
- Crystallinity
  - Amorphous
  - Semi-crystalline
- Polarity

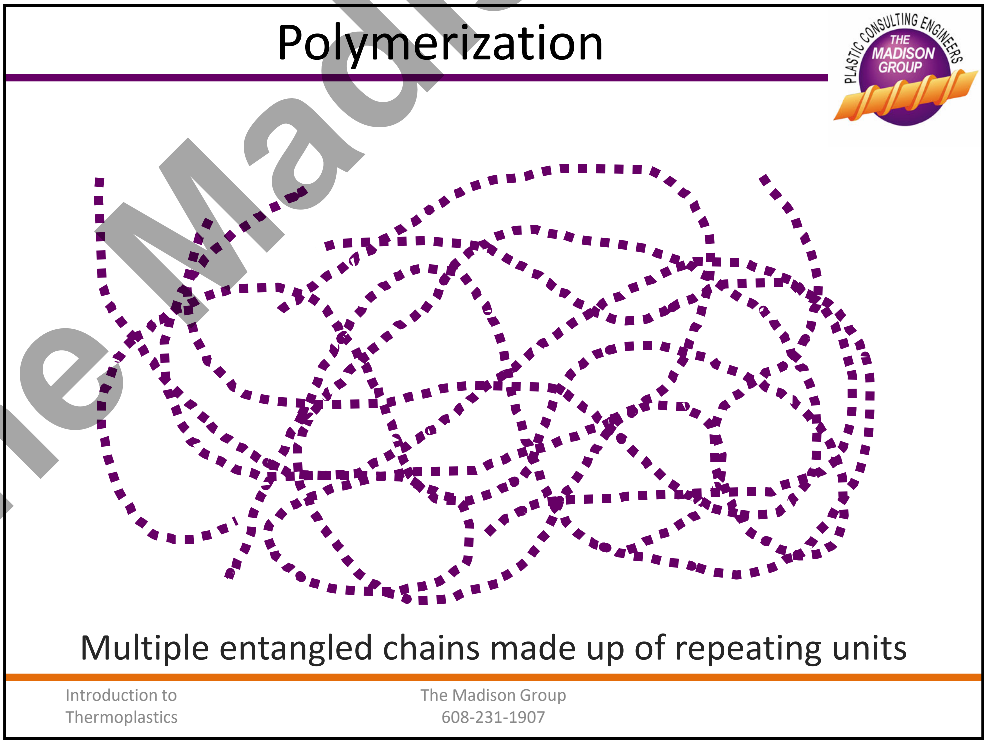
Material Composition

- Base Polymer
  - Functional Groups



Molecular Weight

Polymer chain made up of repeating units

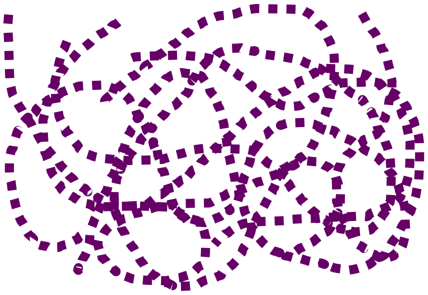


Polymerization

Multiple entangled chains made up of repeating units

Molecular Weight

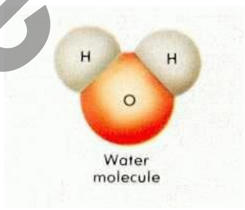
The collection of entangled polymer chains is like a bowl of spaghetti noodles.



Molecular Weight

Molecular Weight: The sum of the atomic weights of the atoms in a molecule.

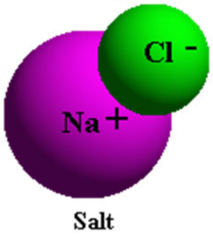
Water



16+1+1=18

Sodium Chloride (Salt)

23+35=58

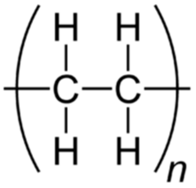


6.02 X10^{23} molecules / mole (molecular weight mass in grams)

Molecular Weight

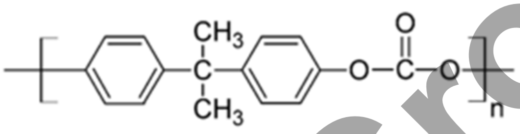
Molecular Weight: The sum of the atomic weights of the atoms in a molecule.

Polyethylene



(12x2 + 1x4) x n

Polycarbonate



(12x16 + 1x14 + 16x3) x n

6.02 X10^{23} molecules / mole (molecular weight mass in grams)

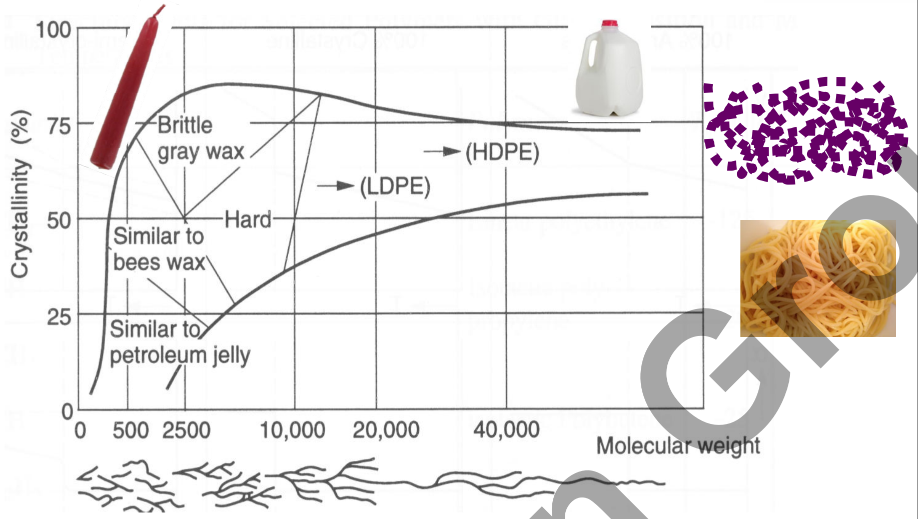
Molecular Weight

Water	1 mole = 18 grams
Sodium Chloride	1 mole = 58 grams
Polyethylene	1 mole = ~500 lbs.
Polycarbonate	1 mole = ~50 lbs.

Most commercial polymers have an average molecular weight between 10,000 and 500,000

6.02 X10^{23} molecules / mole (molecular weight mass in grams)

Molecular Weight



Molecular Weight

Result of Increasing Molecular Weight

Increasing MW
Improves

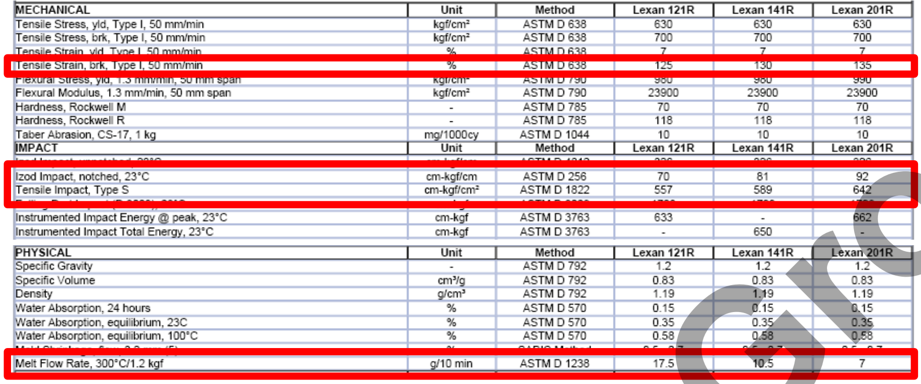
- Tensile Strength
- Elongation at Break
- Yield Strength
- Toughness
- Hardness
- Abrasion Resistance
- Softening Temperature
- Chemical Resistance

Longed molecular chains produce a higher level of entanglement

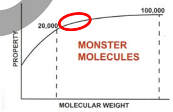
Molecular Weight

Effects of Molecular Weight on Polycarbonate

Increasing MW



MECHANICAL	Unit	Method	Lexan 121R	Lexan 141R	Lexan 201R
Tensile Stress, yld, Type I, 50 mm/min	kgf/cm²	ASTM D 638	630	630	630
Tensile Stress, brk, Type I, 50 mm/min	kgf/cm²	ASTM D 638	700	700	700
Tensile Strain, yld, Type I, 50 mm/min	%	ASTM D 638	7	7	7
Tensile Strain, brk, Type I, 50 mm/min	%	ASTM D 638	125	130	135
Flexural Stress, yld, 1.3 mm/min, 50 mm span	kgf/cm²	ASTM D 790	980	980	990
Flexural Modulus, 1.3 mm/min, 50 mm span	kgf/cm²	ASTM D 790	23900	23900	23900
Hardness, Rockwell M	-	ASTM D 785	70	70	70
Hardness, Rockwell R	-	ASTM D 785	118	118	118
Taber Abrasion, CS-17, 1 kg	mg/1000cy	ASTM D 1044	10	10	10
IMPACT	**Unit**	**Method**	**Lexan 121R**	**Lexan 141R**	**Lexan 201R**
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Izod Impact, notched, 23°C	cm-kgf/cm	ASTM D 256	70	81	92
Tensile Impact, Type S	cm-kgf/cm²	ASTM D 1822	557	589	642
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Instrumented Impact Energy @ peak, 23°C	cm-kgf	ASTM D 3763	633	-	662
Instrumented Impact Total Energy, 23°C	cm-kgf	ASTM D 3763	-	650	-
PHYSICAL	**Unit**	**Method**	**Lexan 121R**	**Lexan 141R**	**Lexan 201R**
Specific Gravity	-	ASTM D 792	1.2	1.2	1.2
Specific Volume	cm³/g	ASTM D 792	0.83	0.83	0.83
Density	g/cm³	ASTM D 792	1.19	1.19	1.19
Water Absorption, 24 hours	%	ASTM D 570	0.15	0.15	0.15
Water Absorption, equilibrium, 23C	%	ASTM D 570	0.35	0.35	0.35
Water Absorption, equilibrium, 100°C	%	ASTM D 570	0.58	0.58	0.58
[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]
Melt Flow Rate, 300°C/1.2 kgf	g/10 min	ASTM D 1238	17.5	10.5	7



Molecular Weight

Effects of Molecular Weight on the Impact Properties of Acetal Copolymer

MFR (g/10min)	Notched Izod (ft-lb/in)	Unotched Izod (ft-lb/in)	Strain @ Break (%)
2.5	1.5	25.0	75
9.0	1.3	20.0	60
27.0	1.0	17.0	40

Longer molecular chains produce a higher level of entanglement

Ref: Mike Sepe

Molecular Weight

Effects of Molecular Weight on the Fatigue Properties of Acetal Copolymer

MFR (g/10min)	Fatigue Strength @ 10^7 Cycles (psi)
2.5	4000
9.0	3300
27.0	3000

Longer molecular chains produce a higher level of entanglement

Ref: Mike Sepe

Molecular Weight

Effects of Molecular Weight on the ESCR of HDPE

MFR (g/10min)	Time to ESC failure (hours)
2	>1000
4	375
6	60
8	10
10	3

Longer molecular chains produce a higher level of entanglement

Ref: Mike Sepe

Plastic Characteristics

Molecular Structure

- Average Molecular Weight
- Molecular Weight Distribution
- Branching
- Tacticity
- Crystallinity
  - Amorphous
  - Semi-crystalline

Material Composition

- Base Polymer
  - Functional Groups
  - Homopolymer / Copolymer

Homopolymer/Copolymer

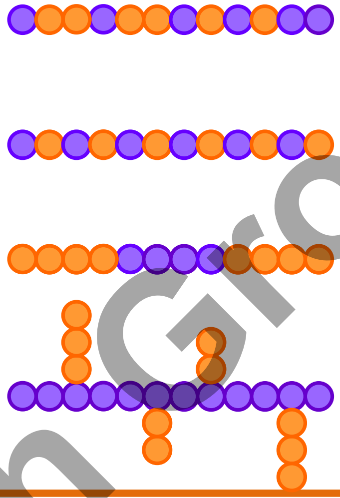
- Polymers that contain only a single type of repeat unit are known as **Homopolymers**.
- Polymers containing a mixture of repeat units are known as **Copolymers**.

A-A-A-A-A-A-A-A-A-A-A-A-A-A-A
homopolymer

A-B-A-B-A-B-A-B-A-B-A-B-A-B-A
copolymer

Homopolymer/Copolymer

- Random copolymers: The monomeric units are distributed randomly, and sometimes unevenly, in the polymer chain.
- Alternating copolymers: The monomeric units are distributed in a regular alternating fashion, with nearly equimolar amounts of each in the chain.
- Block copolymers: Instead of a mixed distribution of monomeric units, a long sequence or block of one monomer is joined to a block of the second monomer:
- Graft copolymers: Side chains of a given monomer are attached to the main chain of the second monomer.

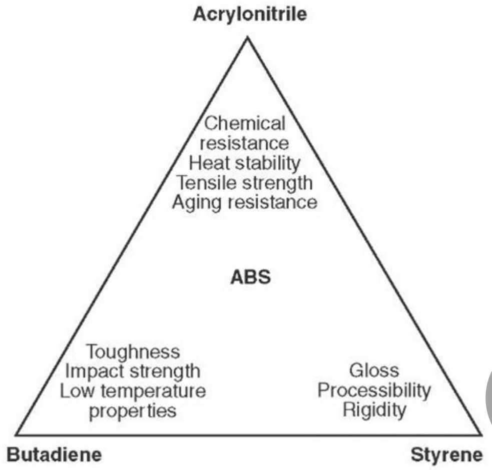


Homopolymer/Copolymer

Copolymerization is used to impart enhanced or unique properties to the material.

- Polypropylene is copolymerized with polyethylene to give the polypropylene better impact resistance and low temperature properties.
- Polyacetal copolymer have superior oxidative stability, chemical resistance, and impact properties.

Homopolymer/Copolymer



Plastic Characteristics

Molecular Structure

- Average Molecular Weight
- Molecular Weight Distribution
- Branching
- Tacticity
- Crystallinity
  - Amorphous
  - Semi-crystalline

Material Composition

- Base Polymer
  - Functional Groups
  - Homopolymer / Copolymer
  - Blends / Alloys

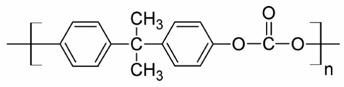
Blends / Alloys

- Polymer Blend: Made by mixing traditional polymers which have already been polymerized . The mixing results in a **multi-phase system**.
- Polymer Alloy: Made by mixing traditional polymers which have already been polymerized. The mixing results in a **single-phase material** because the polymers have some interaction that combines them together.
- Physical interactions between the polymers are responsible for the properties of the final blend or alloy
- Often a distinction between the terms alloys and blends is not made, simply identify whether the material is single or multi-phase.

Blends / Alloys

- Mixing polymers as blends or alloys is a cost-effective way to tailor properties of polymeric materials for specific applications.
- Chemical resistance, impact resistance, weathering, high temperature or low temperature properties,…………
- Commercially available blends and alloys include:
  - polycarbonate/ABS
  - polycarbonate/PET
  - ABS/PVC
  - ABS/polyamide
  - polyphenylene oxide/high impact polystyrene
  - polyphenylene oxide/polyamide
  - polyamide/polyolefin.

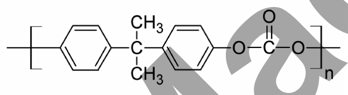
Blends / Alloys



Polycarbonate

- Impact toughness
- Dimensional Stability
- Heat Resistance

Blends / Alloys

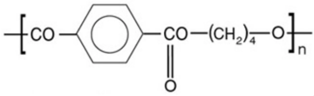


Polycarbonate

- Impact toughness
- Dimensional Stability
- Heat Resistance

<u>CHEMICAL RESISTANCE</u>

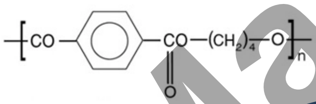
Blends / Alloys



Poly(butyelene terephthalate)

- Chemical Resistance
- High Strength
- High Stiffness
- Flowability

Blends / Alloys

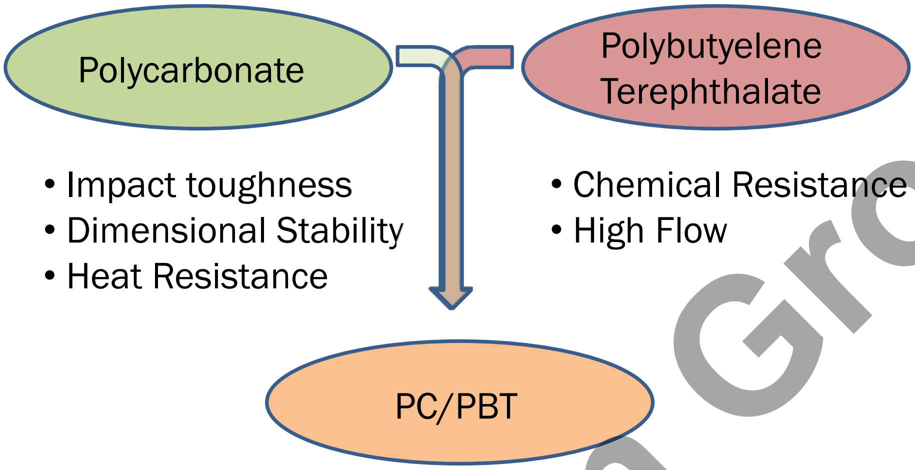


Poly(butyelene terephthalate)

- Chemical Resistance
- High Strength
- High Stiffness
- Flowability

IMPACT RESISTANCE
SHRINKAGE DURING MOLDING

Blends / Alloys



Polycarbonate

Polybutyelene Terephthalate

- Impact toughness
- Dimensional Stability
- Heat Resistance

- Chemical Resistance
- High Flow

PC/PBT

Plastic Characteristics

Molecular Structure

- Average Molecular Weight
- Molecular Weight Distribution
- Crosslinking
  - Thermoplastic
  - Thermoset
- Crystallinity
  - Amorphous
  - Semi-crystalline
- Branching

Material Composition

- Base Polymer
  - Functional Groups
  - Homopolymer / Copolymer
  - Blends / Alloys
- Additives
  - Modifiers
  - Anti-degradants
  - Colorants
  - Fillers

Additives

- **Flame Retardants**

  Additives that inhibit or resist the spread of fire by a)increasing plastic's ignition resistance, b) reducing the speed of flame spread, c) reducing heat release, or d) reducing smoke & fume generation.

- **Anti-degradants and Stabilizers**

  Additives to prevent various molecular degradation effects such as oxidation, hydrolysis, chain scission chain and uncontrolled destructive cross-linking reactions that are caused by thermal, chemical or weathering exposure.

Additives

- **Colorants**

  Additives (pigments and dyes) that change the look of the plastic to the human eye. Dispersed in plastics to provide characteristics such as color, fluorescence, gloss, hiding power, and color durability.

- **Plasticizers**

  Additives that embed themselves between the chains of polymer, spacing them apart and increasing the free volume. This decreases the glass transition, resulting in increased softening and flexibility.

Additives

- **Fillers and Reinforcements**

  Additives that are relatively inexpensive, solid substances that are added in fairly high concentrations to adjust volume, weight, costs, or technical performance.

Additives

- Reinforcing fillers improve the mechanical properties of the plastic.
  - Fibers and high aspect ratio minerals: glass fiber, Kevlar fiber, carbon
- Non-reinforcing fillers add bulk to the plastic compound and reduce cost.
  - Low aspect materials: glass beads, kaolin clay, talc, calcium carbonate, silica

Additives

- **Nucleating Agents and Calrifiers**
  Additives used to provide the processor with increased control over the initiation and progression of crystallization. They are used to affect the physical and optical properties of the material.

- **Specialty Additves**
  - Friction Control: PTFE and MoS_2
  - Antimicrobials
  - Process Aids
  - Slip Agents
  - Blowing Agents
  - Conductivity

THANK YOU

Questions?

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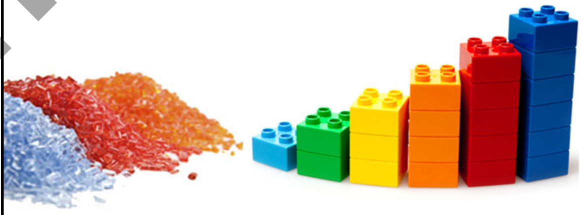


Degradation Failure of Plastics

Jeffrey A. Jansen
January 21, 2021

Agenda

- Introduction to Polymer Degradation
- Failure of Plastics
- Degradation Mechanisms
  - Thermal Oxidation
  - Chain Scission
  - Hydrolysis
  - Photo Oxidation
- Degradation Stabilization
- Assessing Molecular Degradation
- Failure Case Illustrations

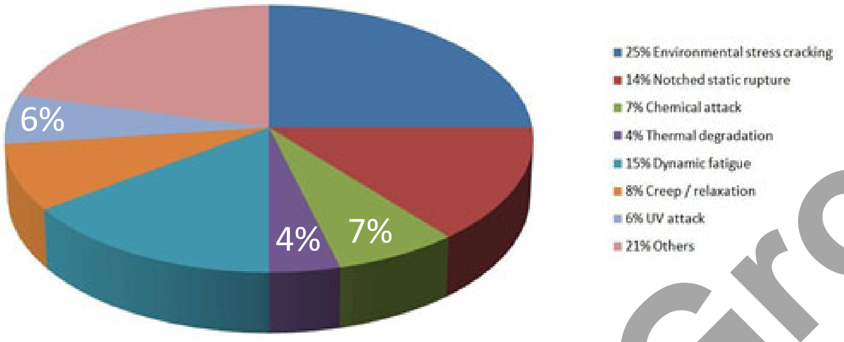
INTRODUCTION TO DEGRADATION

Molecular Degradation

Molecular Degradation is...

deleterious alteration of the molecular structure within a polymeric material as the result of a chemical reaction

Molecular Degradation



Taken From " Failure of Plastics and Rubber Products" by David Wright

Molecular Degradation

Molecular Degradation Mechanisms

- Oxidation
- Ultraviolet Radiation (UV)
- Hydrolysis
- Chain Scission
- Side Chain Alteration
- Destructive Crosslinking

Any point in the material life cycle

Molecular Weight Changes Permanently Through Chemical Reactions

Molecular Degradation

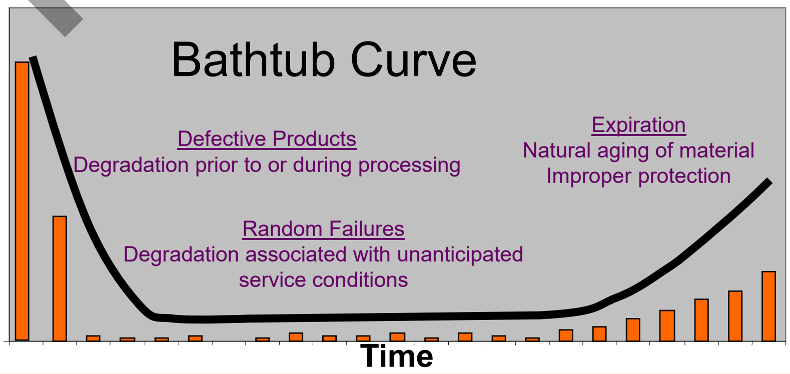
Molecular Degradation Mechanisms

- Compounding
  - Exposure to elevated shear induced heating while additive are incorporated into compound
- Drying
  - Exposure to extreme time/temperature profile in drying hopper
- Processing
  - Insufficient drying of resin prior to injection molding
- Storage
  - Exposure of polymeric tubing to sunlight prior to installation
- Installation
  - Elevated temperature use for welding operation
- Service
  - Contact with aggressive acid or alkaline cleaning chemical agents

Molecular Degradation

Product Life Cycle

Degradation Failure Over Time



Molecular Degradation

Plastic Failure Categories

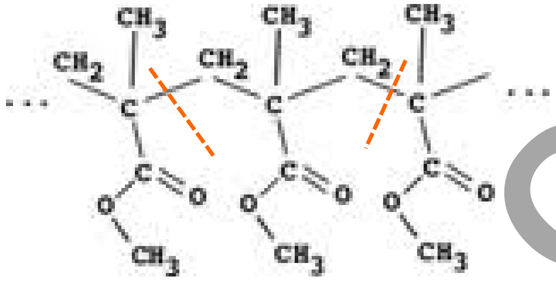
- Deformation / Distortion
- Esthetic Alteration
- Degradation
- Wear
- Fracture

CRACKING IN PLASTICS

Plastics Cracking

Characteristics of Plastics Cracking:

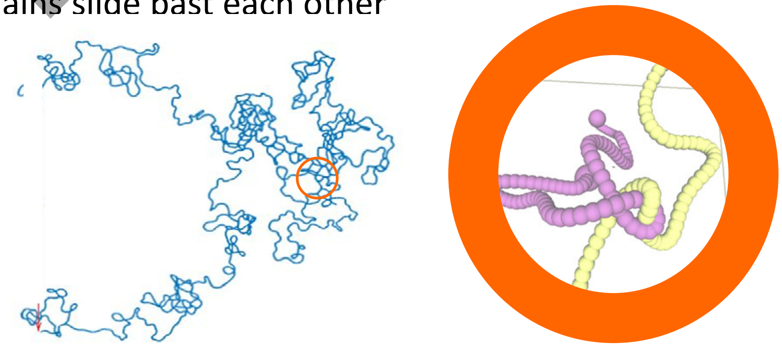
- Covalent polymer backbone bonds are not broken by mechanical forces



Plastics Cracking

Characteristics of Plastics Cracking:

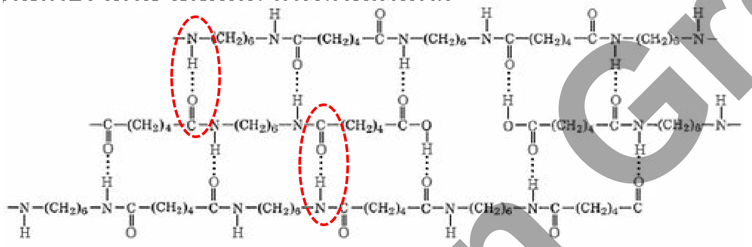
- Disentanglement mechanism in which polymer chains slide past each other



Plastics Cracking

Characteristics of Plastics Cracking:

- Applied stresses – both internal and external - overcome inter-molecular forces such as, Van der Waals forces, London dispersion forces, hydrogen bonding, and dipole interactions

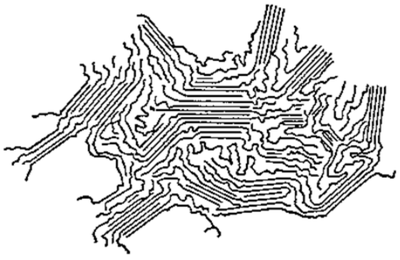


Plastics Cracking

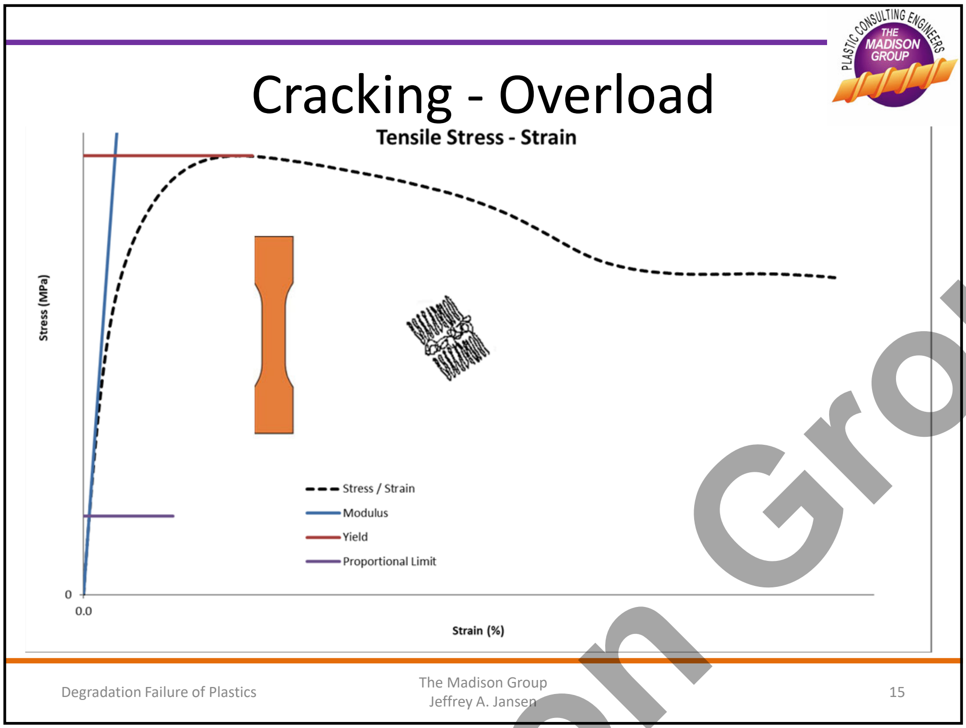
Characteristics of Plastics Cracking:

- Mechanism is the same for amorphous and semi-crystalline polymers

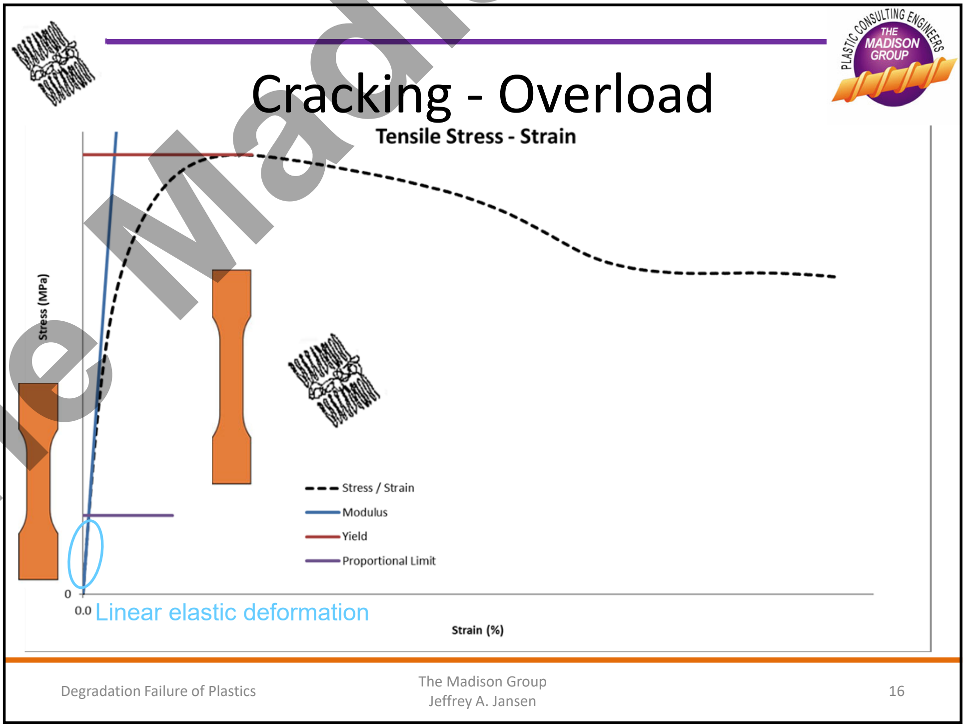
Amorphous



Semi-crystalline

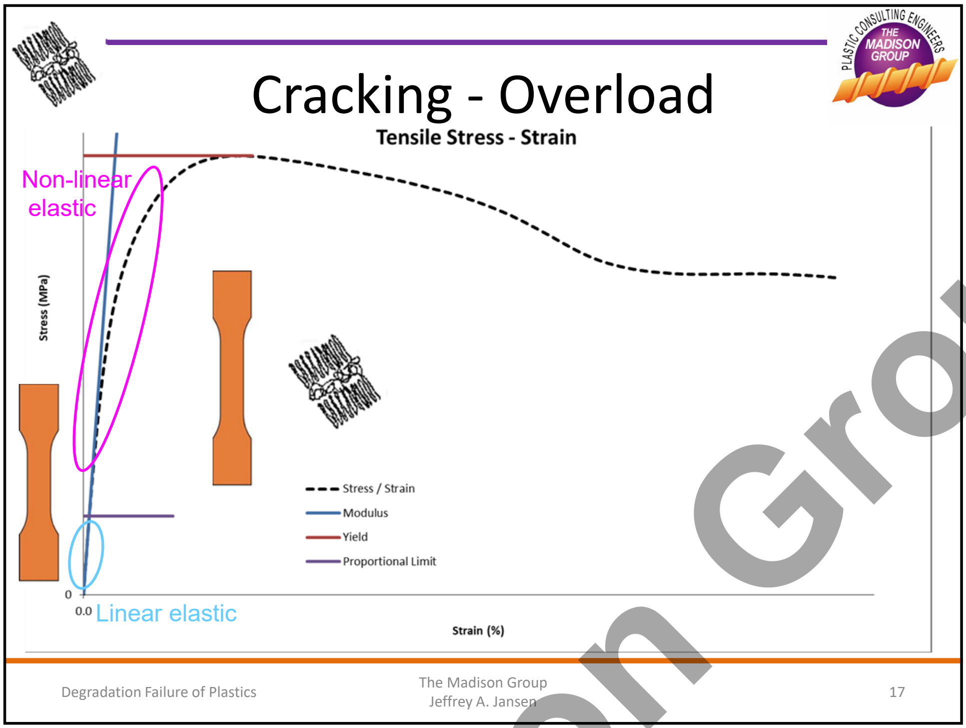


Cracking - Overload



Cracking - Overload

Linear elastic deformation



Cracking - Overload

Degradation Failure of Plastics

The Madison Group
Jeffrey A. Jansen

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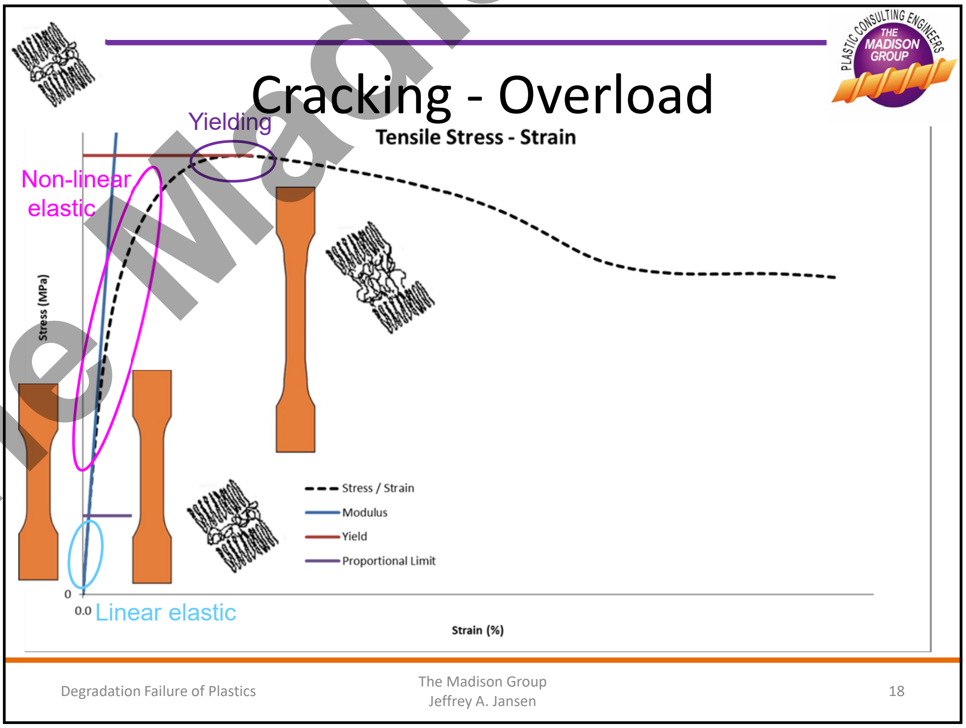

Cracking - Overload

Degradation Failure of Plastics

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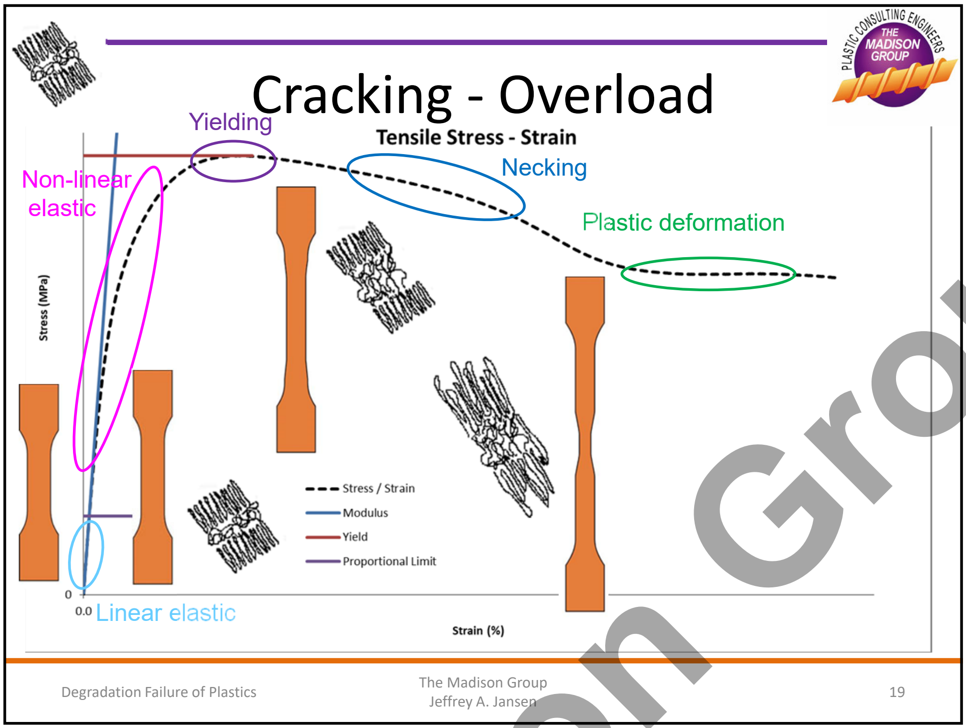

Cracking - Overload

Degradation Failure of Plastics

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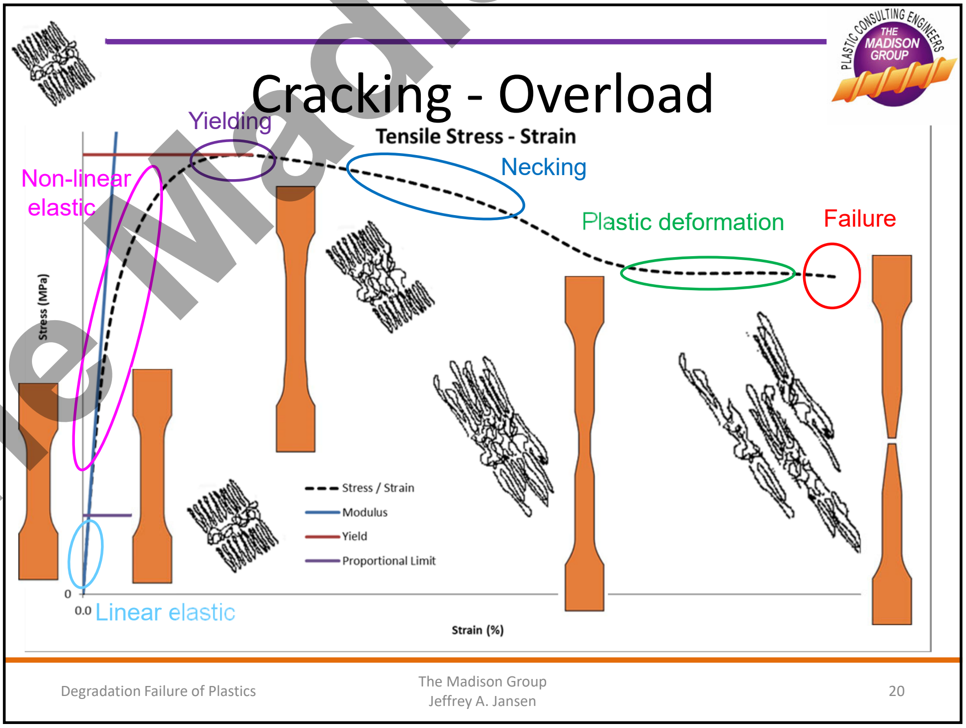

Cracking - Overload

Degradation Failure of Plastics

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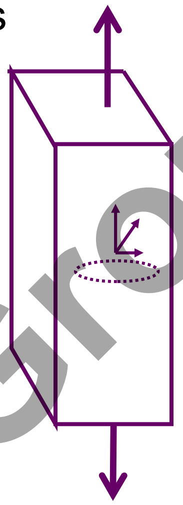
Plastics Cracking

Cracking is Simply a Response to Stress

- Cracking occurs as a stress relief
- Ductile fracture is a bulk molecular response through yielding (macro molecular rearrangement) followed by disentanglement
- Brittle fracture is a localized molecular response where disentanglement is favored over yielding



Plastics Cracking

Plastic Ductile-to-Brittle Transitions

Production

- Low Molecular Weight Material Selection
- Poor Fusion / Molecular Entanglement
- Contamination
- Increased Filler Level
- Stress Concentration – Design or Defects
- *Molecular Degradation*

Service

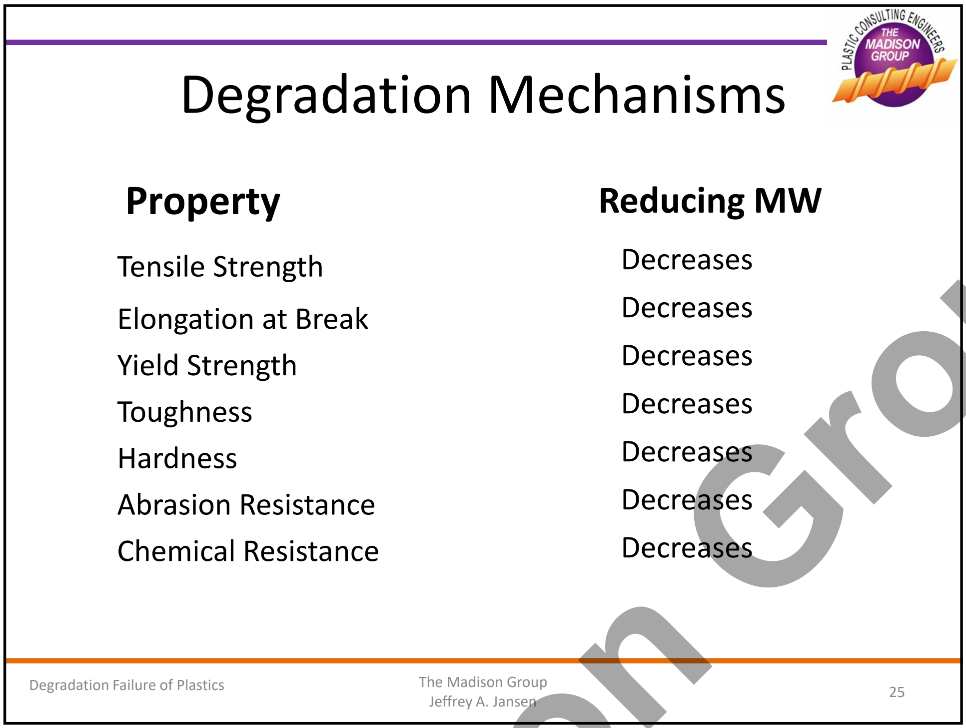
- Reduced Temperature
- Elevated Strain Rate
- Extended Time Under Stress
- Cyclic Loading
- Chemical Exposure
- Loss of Plasticizer
- *Molecular Degradation*

DEGRADATION MECHANISMS

Degradation Mechanisms

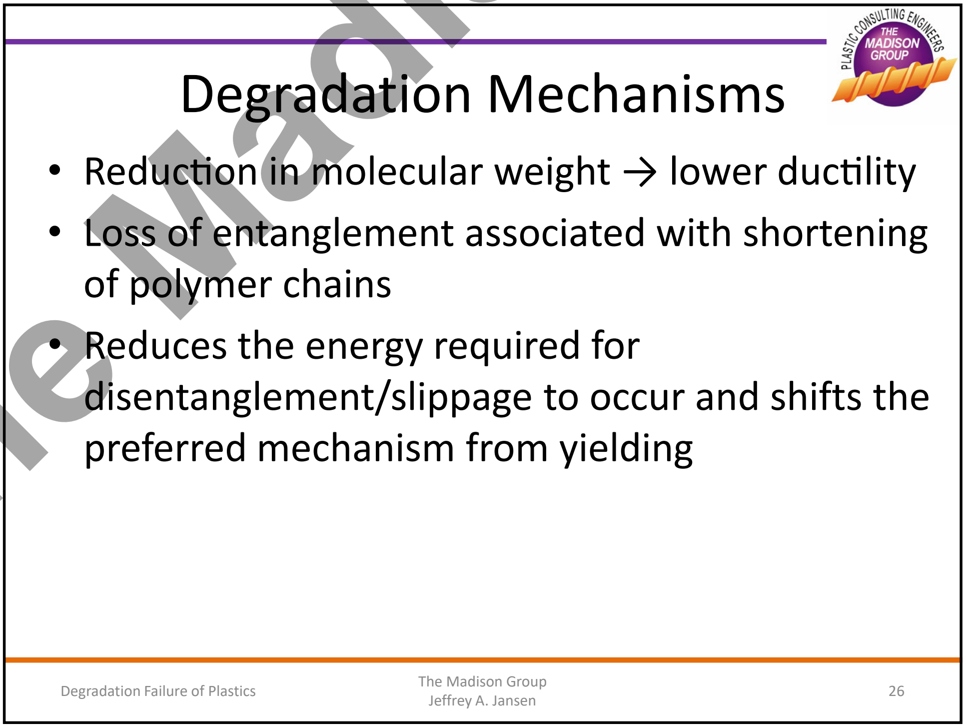
The dominant mechanism of molecular degradation and the extent of degradation is dependent on the polymer and application environment. The results are the same for most polymer families and significant property degradation can occur when any type of degradation occurs.

All forms of degradation represent chemical reactions that result in molecular structural changes.



Degradation Mechanisms

Property	**Reducing MW**
Tensile Strength	Decreases
Elongation at Break	Decreases
Yield Strength	Decreases
Toughness	Decreases
Hardness	Decreases
Abrasion Resistance	Decreases
Chemical Resistance	Decreases



Degradation Mechanisms

- Reduction in molecular weight → lower ductility
- Loss of entanglement associated with shortening of polymer chains
- Reduces the energy required for disentanglement/slippage to occur and shifts the preferred mechanism from yielding

THERMAL OXIDATION

Thermal Oxidation

Thermal Oxidation is …..

degradation of a polymeric material through contact with an chemical oxidizer

chemical reaction in which oxygen is introduced into the molecular structure of the polymer

Thermal Oxidation

Thermal Oxidation

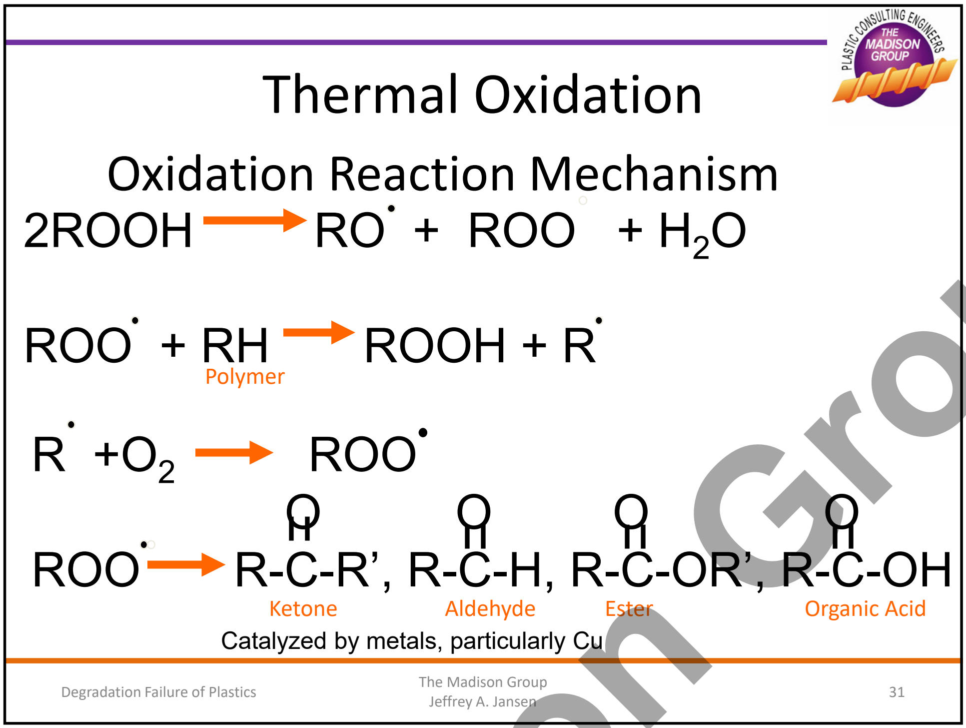
The rate of the degradation reaction increases with increasing temperatures – follows the Arrhenius Rate Law

The oxygen in the air is the reactant and ambient heat is the energy source which drives the reaction

Thermal Oxidation

Thermal Oxidation

- Most polymers undergo thermal oxidation.
- Oxidation takes places via free radical formation.
- Chemical reaction – incorporation of oxygen into the backbone structure, creates carbonyl structural groups.



Thermal Oxidation

Oxidation Reaction Mechanism

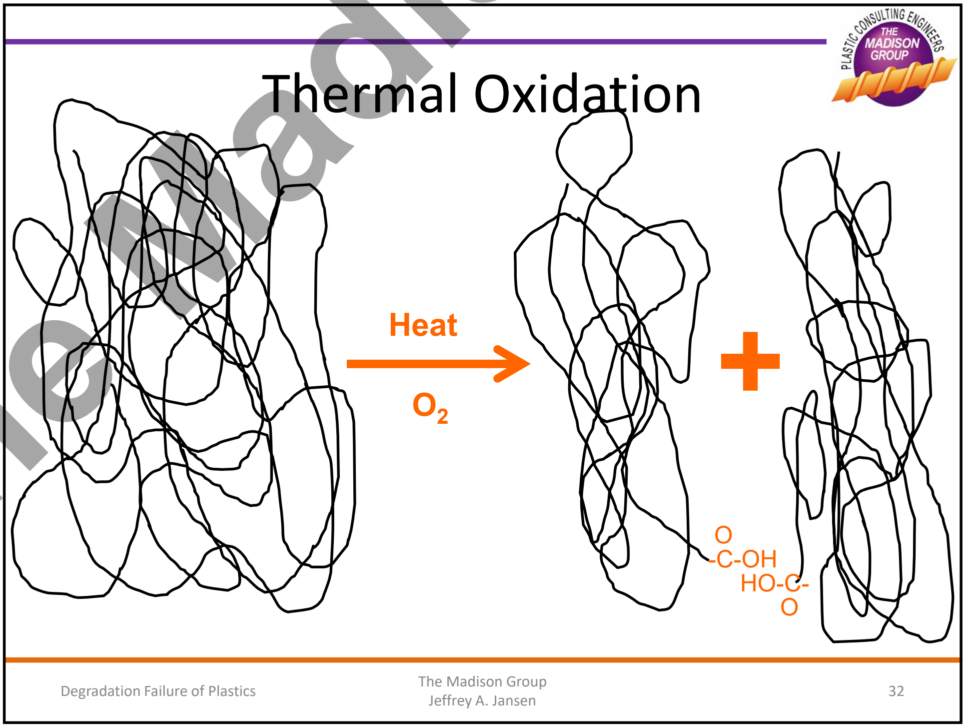
$$2ROOH \rightarrow RO^{\bullet} + ROO + H_2O$$

$$ROO^{\bullet} + \underset{\text{Polymer}}{RH} \rightarrow ROOH + R^{\bullet}$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$

$$ROO^{\bullet} \rightarrow \underset{\text{Ketone}}{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}R'},\ \underset{\text{Aldehyde}}{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}H},\ \underset{\text{Ester}}{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR'},\ \underset{\text{Organic Acid}}{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH}$$

Catalyzed by metals, particularly Cu



Thermal Oxidation

Thermal Oxidation

Effects of Oxidation

- Loss of Molecular Weight
  - Embrittlement
  - Loss of Mechanical Integrity
  - Cracking
  - Catastrophic Failure
- Conjugation
  - Discoloration
  - Loss of Gloss
  - Loss of Transparency
- Evolution of Volatiles
  - Foul Odor Generation
- Carbonyl Formation
  - Loss of Dielectric Properties

Thermal Oxidation

Termination of Oxidation Reaction

$2R^{\bullet} \rightarrow$ R-R (Destructive Crosslinking)
$ROO^{\bullet} + R^{\bullet} \rightarrow$ ROOR (Unstable)
$2ROO^{\bullet} \rightarrow$ Non-Radical Products

Termination of the reaction forming non-radical species non-destructively generally requires the use of additives.

Thermal Oxidation

Key Factors

- Polymer Type
  - Molecular structure of the polymer
  - Functional Groups
  - Branching
- Formulation Additives
  - Type
  - Effectiveness
- Strength of oxidizing chemical
- Temperature
- Exposure Time
- Stress Level (Internal and External)

Thermal Oxidation

Decreasing Susceptibility to Oxidation

Polypropylene
Low Density Polyethylene
High Density Polyethylene
Nylon
Polyacetal
Poly(phenylene oxide)
Poly (ether ether ketone)
Poly(phenylene sulfide)
Poly(vinylidene fluoride)
Polytetrafluoroethylene

CHAIN SCISSION

Chain Scission

Chain Scission is …..

degradation of a polymeric material in the absence of a chemical agent (no air)

chemical reaction in which the molecular structure of the polymer is altered solely based on thermal energy - **absence of oxygen drives the mechanism**

Chain Scission

Chain Scission

Caused by exposure to elevated temperature in combination with high shear stress

Usually associated with processing techniques

Chain Scission

Chain Scission Reaction Mechanism

$$\mathbf{R - R \longrightarrow R1 \quad + \quad R2}$$

HYDROLYSIS

Hydrolysis

Hydrolysis is …..

degradation of a polymeric material through contact with water - the hydrogen cations (H^+) or hydroxyl anions (OH^-)

contact with acids (high H^+ concentration) or bases (high OH^- concentration) can dramatically accelerate hydrolysis

Hydrolysis

Hydrolysis Reaction Mechanism

$$R-\overset{O}{\overset{\|}{C}}-O-R1 + H_2O \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + R1-OH$$

Some polymers produce water as a by-product of hydrolysis

Hydrolysis

Hydrolysis

Different than water absorption

Hydrolysis

Hydrolysis

- Water
- Condensation
- Steam
- Acids and alkalis

Hydrolysis

Hydrolysis - Susceptible Polymers

- Polyesters (PBT, PET)
- Polycarbonate (PC)
- Nylon (PA6, PA6/6, PA12, ….)
- Polyimide (PI)
- Polyacetal (POM)

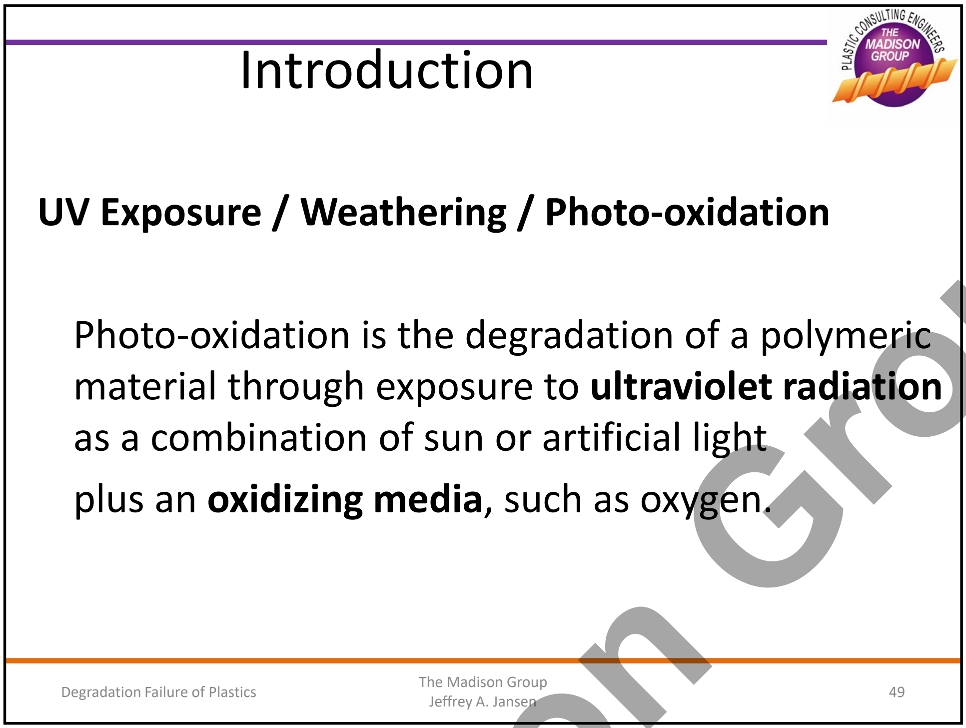
Condensation Polymerization

Hydrolysis

Tensile stresses of a few MPa, can increase the rate of hydrolysis by a factor of 10.

- Stress enhanced diffusion
- Mechanically induced chain scission
- Stress separation of chain ends precluding chain recombination

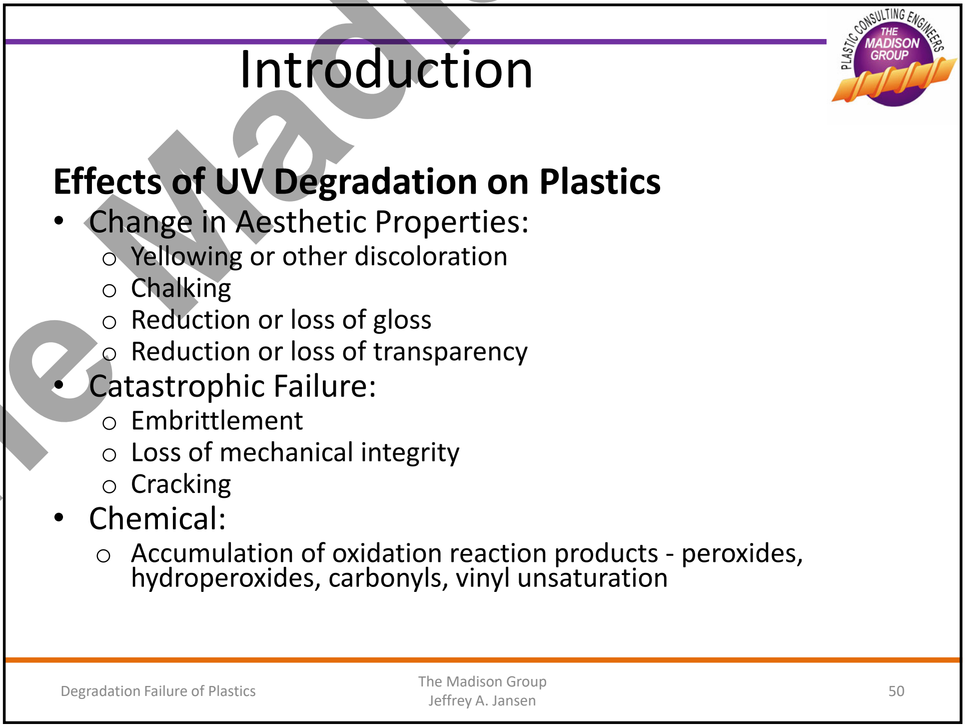
PHOTO-OXIDATION



Introduction

UV Exposure / Weathering / Photo-oxidation

Photo-oxidation is the degradation of a polymeric material through exposure to **ultraviolet radiation** as a combination of sun or artificial light plus an **oxidizing media**, such as oxygen.



Introduction

Effects of UV Degradation on Plastics

- Change in Aesthetic Properties:
  - Yellowing or other discoloration
  - Chalking
  - Reduction or loss of gloss
  - Reduction or loss of transparency
- Catastrophic Failure:
  - Embrittlement
  - Loss of mechanical integrity
  - Cracking
- Chemical:
  - Accumulation of oxidation reaction products - peroxides, hydroperoxides, carbonyls, vinyl unsaturation

Photo-oxidation Mechanism

Effects of UV Degradation on Plastics

The degradation depth is usually confined to the exposed surface layer. - approximately 100 µm

This is controlled by the diffusion of oxygen

- Formation of a brittle surface layer
- Shrinkage of the degraded surface layer
- Cracking within the surface layer
- Cracks extend to unaffected base material – brittle fracture

Photo-oxidation Mechanism

The photo oxidation degradation mechanism is similar to thermal oxidation, excpet initaed and accelerated by UV radiation.

UV radiation results in the cleavage of chromophores

Initiation Step:

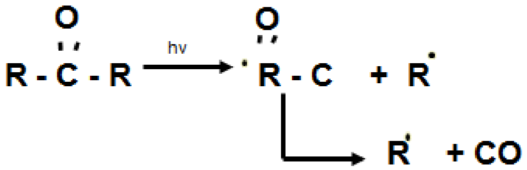
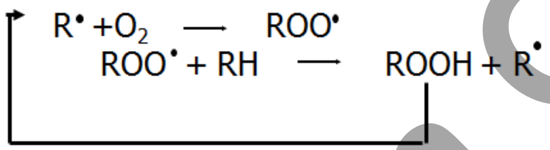


Photo-oxidation Mechanism

Chain reaction of polymer radicals with O_2 through Oxidation

Free radicals formed through the decomposition of hydroperoxides react with oxygen.

Propagation Step:



$$R^\bullet + O_2 \longrightarrow ROO^\bullet$$

$$ROO^\bullet + RH \longrightarrow ROOH + R^\bullet$$

Photo-oxidation Mechanism

Nonradical species decompose to produce multiple free radicals.

Rapid reaction acceleration at this stage.

Autocatalysis Step:

$$2ROOH \longrightarrow RO^\bullet + ROO^\bullet + H_2O$$

Photo-oxidation Mechanism

Termination - Stopping the Free Radical Propagation

(A) $2R^{\bullet} \longrightarrow R\text{-}R$ (Destructive Crosslinking)
(B) $ROO^{\bullet} + R^{\bullet} \longrightarrow ROOR$ (Peroxides)
(C) $2ROO^{\bullet} \longrightarrow$ Non-Radical Products

Termination to form non-radical products terminates reaction non-destructively. Usually due to the use of additives

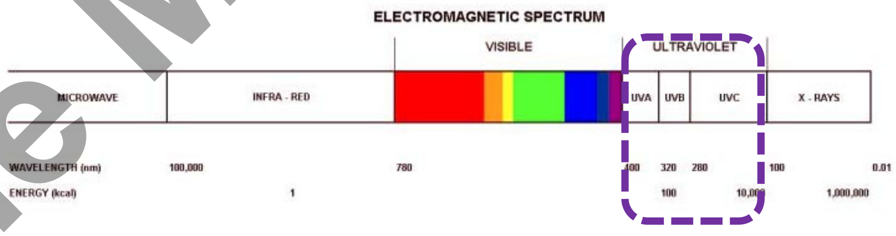
Photo-oxidation Mechanism

- The reduction in molecular weight associated with degradation produces small cleaved molecules. These small molecules easily crystallize resulting a local increase in polymer density.
- The material density increases because of carbonyl formation and revised crystal structure. This produces shrinkage of the material, which in turn leads to cracking.
- The strain induced in the molecular structure renders the molecules even more prone to further oxidation.
- The low molecular weight material formed through oxidation is low in tie molecules. Reduces the resistance to crack propagation.

Photo-oxidation - Subject Bonds

- The shorter UV wavelengths / highest energy are the most aggressive toward polymeric materials.
- UV energy at short wavelengths that are natural in nature (295 nm) can break molecular bonds:
  - C-N
  - O-O
  - C-Cl
  - C-O
  - N-H
  - Si-O

Photo-oxidation Light Spectrum



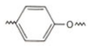
Materials

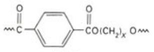
Photo-oxidation Materials

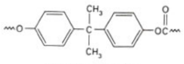
- Photo-oxidative degradation is generally initiated at a location within the material where UV energy is absorbed, known as a **Chromophore**
  - On the polymer chain
  - At a molecular defect within polymer
  - Within a formulation constituent or contaminant

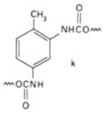
Photo-oxidation Materials

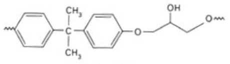
Chromophore in Polymer Structure

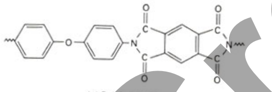

(k) Polyphenylene ether (PPE)

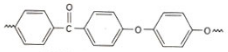

(l) Polyester


(m) Polycarbonate (PC)


(n) Polyurethane (PUR)


(o) Bisphenol A epoxy


(p) Polyimide (PI)


(q) Polyetheretherketone (PEEK)

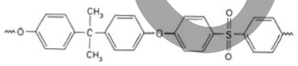
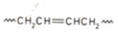
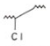

(r) Polysulfone (PSU)

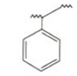
Photo-oxidation Materials

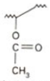
***NO* Chromophore in Polymer Structure**

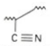

(a) Polyethylene (PE)

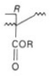

(b) Polybutadiene

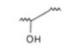

(c) Polyvinyl chloride (PVC)

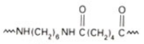

(d) Polystyrene (PS)


(e) Polyvinyl acetate


(f) Polyacrylonitrile


(g) Polymethacrylate


(h) Polyvinyl alcohol (PVAL)


(i) Polyamide (PA)

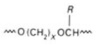

(j) Polyacetal

Photo-oxidation Materials

Chromophore on the polymer chain

- Polycarbonate (PC), poly(phenylene oxide) (PPO), polysulfone (PSU, PESU, PPSU) absorb in the near UV range, 290 to 350 nm
- This poses a significant challenge for UV stabilization

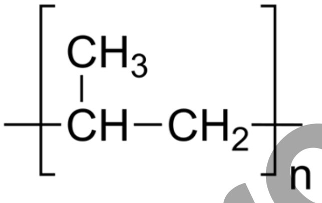
Photo-oxidation Materials

Structural anomaly within polymer

- The structure of polyethylene (PE) and polypropylene (PP) are photo-stable. HOWEVER, these materials can undergo chemical changes during polymerization, molding, storage that can produce carbonyl and hydroperoxide functional groups, rendering them susceptible.
- Poly(vinyl chloride) and acrylic resins are subject to chemical anomalies making these materials susceptible.

Polypropylene

- The presence of hydroperoxides arises from oxidation associated with polymerization, molding, or service.
- Photo-oxidation occurs through excitation of hydroperoxides and subsequent breakdown and the formation of free radicals.
- Thought to process through the general oxidation mechanism.
- Polypropylene highly susceptible to oxidation.
- Photo-oxidation byproducts include organic acids and esters.



$$\left[\begin{array}{c} CH_3 \\ | \\ -CH-CH_2- \end{array} \right]_n$$

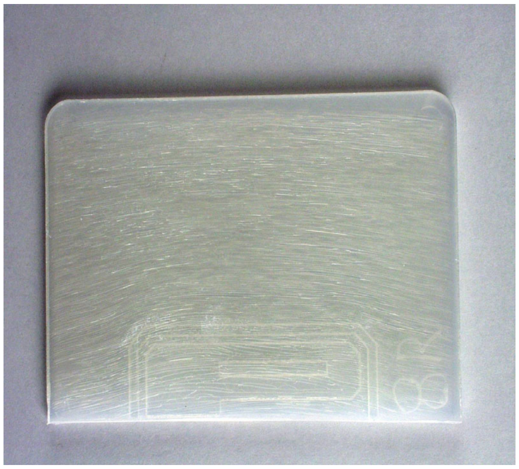
Polypropylene

Polypropylene Copolymer

UV exposure at nominal 25 °C over 1000 hours.

Image through permission of Society of Plastics Engineers (SPE).
Webinar Ultraviolet (UV) Effects on Plastics - January 28, 2010

Polypropylene



Visual Examination

- Cracking present on both sides, but most severe damage on the exposed surface

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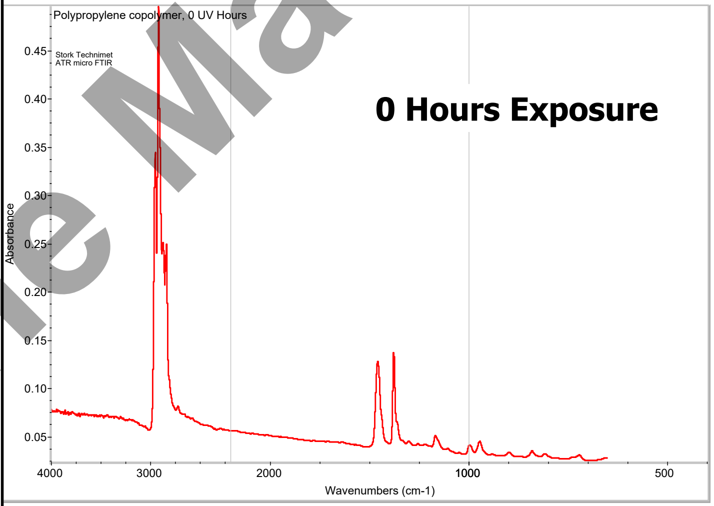
Polypropylene



FTIR Analysis

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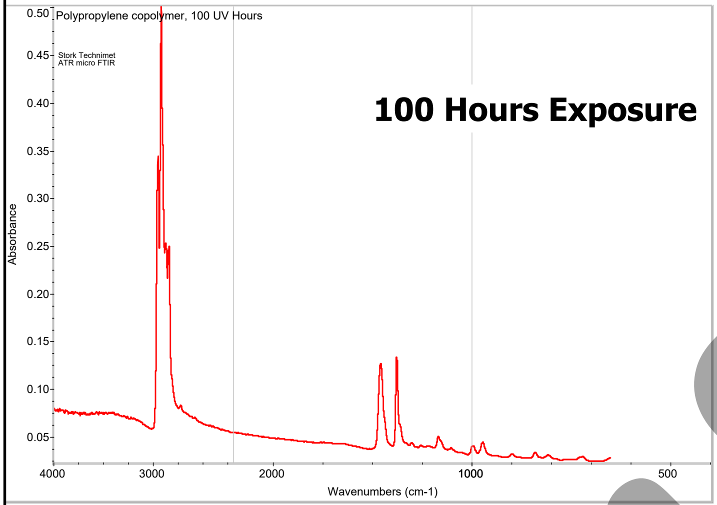
Polypropylene



100 Hours Exposure

FTIR Analysis

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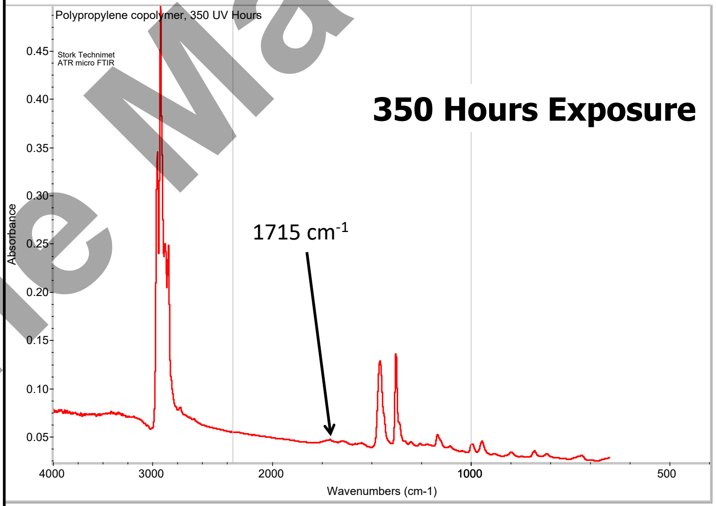
Polypropylene



350 Hours Exposure

Oxidation evident associated with carbonyl formation

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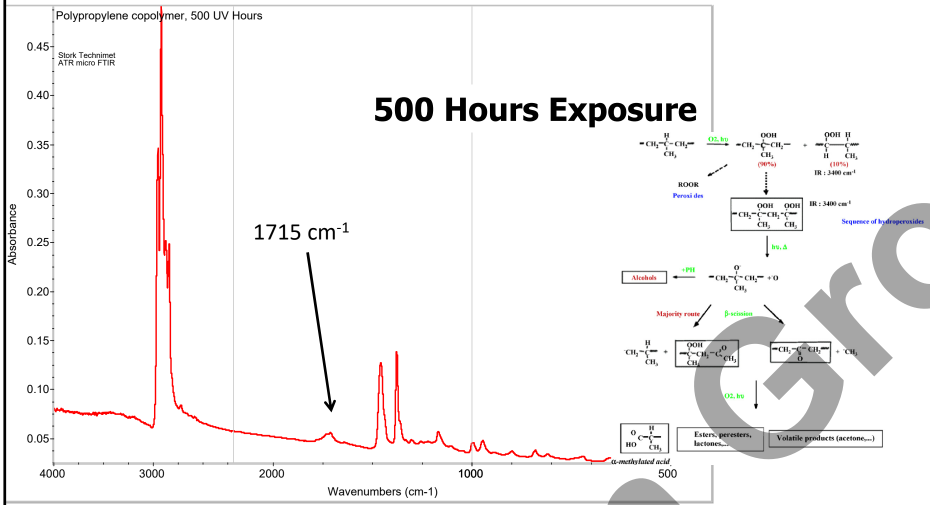
Polypropylene



500 Hours Exposure

1715 cm^{-1}

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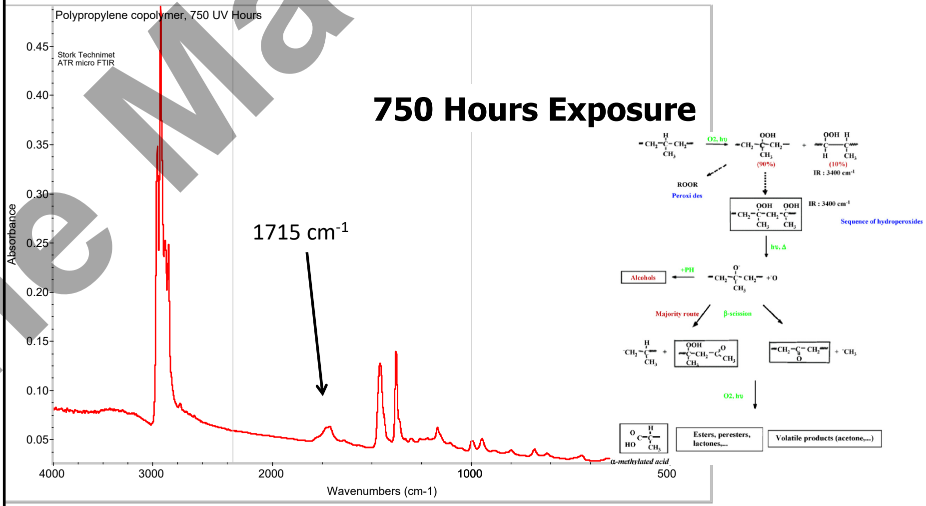
Polypropylene



750 Hours Exposure

1715 cm^{-1}

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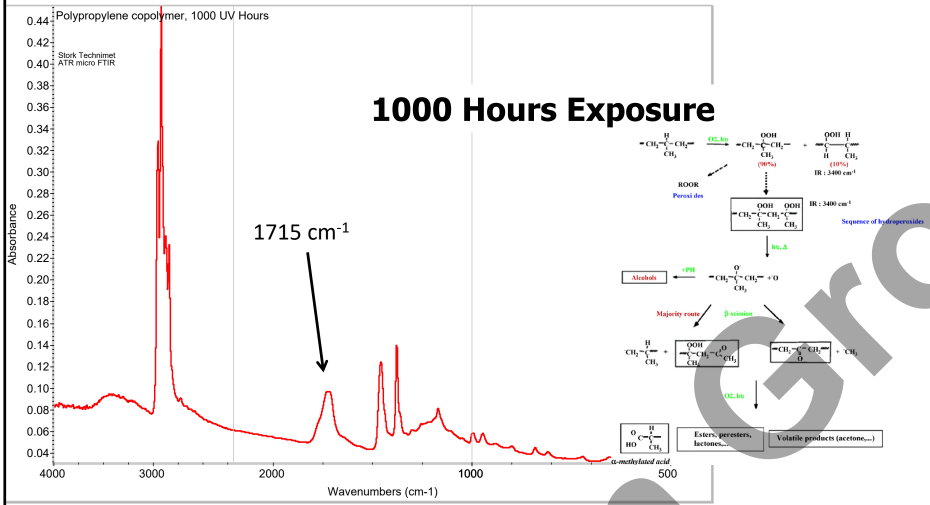
Polypropylene



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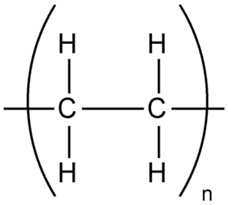
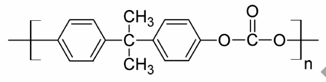
Polyethylene

- Less sensitive to photo-oxidation than polypropylene - slightly more resistant to oxidation.
- However, UV exposure in air results in molecular degradation.
- Photo-oxidation initiates due to residual metal ions left as catalyst residue or from oxidation products formed through molding degradation.
- General photo-oxidation follows hydroperoxide / free radical reaction pattern.
- Copolymer with vinyl acetate (EVA) can decrease resistance. Acetate functionality is a chromophore.
- Photo-oxidation products include vinyl alkenes, ketones, organic acids, and esters.

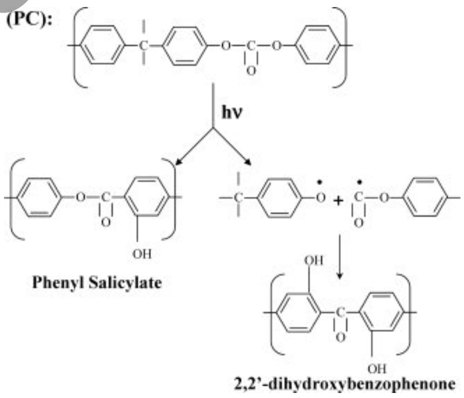


Polycarbonate

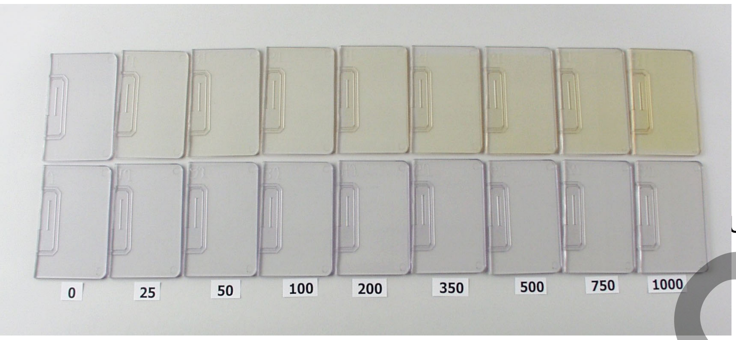
- Polycarbonate begins to absorb UV light at 360 nm and below.
- Intensive absorption around 300 nm.
- Most studies have been conducted using artificial light – many confirmed though outdoor exposure.
- Short wavelength photolysis results in formation of dihydroxybenzophenone.
- Causes yellowing due to absorption within the visible spectrum.
- Photo-oxidation byproducts allow water penetration leading to further degradation through hydrolysis.
- Combined UV exposure and water contact over prolonged time allows hydrolysis to substantially accelerate the photo-oxidation.



Polycarbonate



Polycarbonate



Standard Grade

UV Resistant Grade

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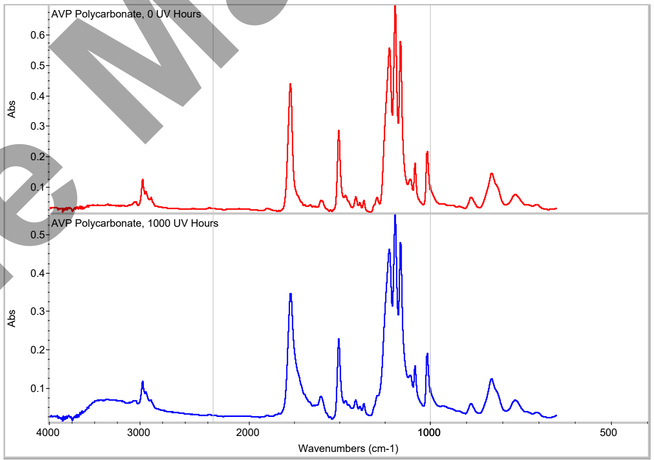
Webinar Ultraviolet (UV) Effects on Plastics - January 28, 2010

Polycarbonate

FTIR

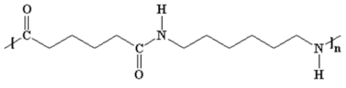


After 1000 hours of UV exposure a broadening of the carbonyl band and the formation of hydroxyl functionality was apparent – Evidence of dihydroxybenzophenone.

Image through permission of Society of Plastics Engineers (SPE). Webinar Ultraviolet (UV) Effects on Plastics - January 28, 2010

Nylon

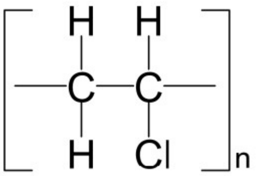
- Nylon absorbs only slightly in the short wavelength of sunlight.
- More absorption than polypropylene or polyethylene.
- At wavelengths up to 340 nm, the amide structure will absorb energy. Amide group is a chromophore.
- Most absorption attributed to impurities in the material. Keto-imide intermediate remaining from polymerization thought to be primary agent to initiate photo-oxidation.
- The absorption of moisture puts water into contact with the molecular structure. This results in combined hydrolysis and photo-oxidation. Significnatly speeds degradation.



nylon 6,6

Poly(vinyl chloride)

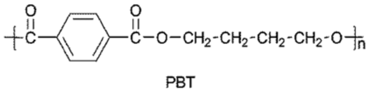
- Pure PVC does not absorb UV radiation above 220 nm – no chromophore in structure.
- Functional groups produced during polymerization and processing and present as contamination are responsible for initiating degradation. Chromophores – hydroperoxides, carbonyl groups, and unsaturation.
- Ester-based plasticizers in flexible PVC can also oxidize – initiate degradation mechanism.
- Photo-oxidation of PVC generates hydrochloric acid. Can degrade adjacnet materials.
- Discoloration and reduction of mechanical properties takes place.



$$\left[\begin{array}{c} \mathrm{H} \quad \mathrm{H} \\ -\mathrm{C}-\mathrm{C}- \\ \mathrm{H} \quad \mathrm{Cl} \end{array} \right]_n$$

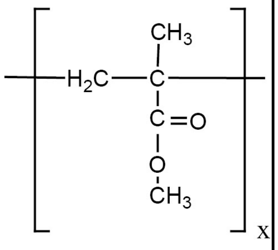
Polyesters

- Polyesters absorb UV radiation below 360 nm.
- Byproducts of photo-oxidation include carboxylic acids, carbon monoxide, and carbon dioxide – oxides of carbon.
- Follows general radical formation mechanism.



Acrylics

- Acyclic resins demonstrate outstanding light and UV stability.
- Any residual methyl methacrylate monomer increases the degradation initiation rate.
- Only minor absorption above 290 nm in the pure resin.
- Commercial resins absorb at 330 nm and lower, due to formulation additives and contaminants.
- Green light at 540 nm known to cause degradation.
- Radical formation through the decomposition of ester functionality.
- Photo-oxidation can occur with or without oxygen – oxidizing media produced through UV degradation.

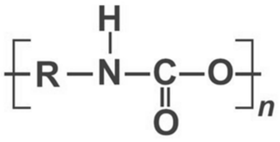


Acrylics

Acrylic coating over polycarbonate lens.

Polyurethane

- Photo-oxidation of urethanes results in discoloration/yellowing and reduction in mechanical properties.
- Degradation through exposure to UV radiation between 335 nm and 410 nm.
- Scission of N-C bonds and C-O bonds
- Degradation progresses through standard hydroperoxide and free radical formation.



$$\left[R-\overset{H}{\overset{|}{N}}-\underset{O}{\underset{\|}{C}}-O \right]_n$$

Photo Oxidation - Initiation Site

- UV molecular degradation initiates at a chromophore – 3 primary sources.

- Polymers in which the chromophore responsible for UV absorption is within the main chain structure - PC, PPO, PSU.
- Polymers in which chemical changes occur during manufacturing, processing, storage or use that result in the formation of carbonyl and hydroperoxide functionality - PE, PP.
- Polymers whose photochemistry is controlled exclusively by chemical anomalies - PVC, PMMA.

Stabilization

Stabilizers

Primary UV Stabilization Strategies

- UV Absorption
- Quenching
- Hydroperoxide Decomposition
- Free Radical Scavenging
- Hindered Amine Light Stabilizers

UV Absorption

- Based on formulation additives, the absorption of UV radiation and subsequent dissipation, most often as as heat.
- Additive compounds must be light stable, or they will be consumed too quickly.
- Generally not effective on thin parts - require a critical penetration depth.
- Hydroxybenzophenones and hydroxyphenylbenzotriazoles are most commonly used.
- Titanium dioxide can also be used – requires very high quality.

Quenching

- Light stabilizer additives are that take the energy that would be absorbed by the chromophores, and dispose of it. This prevents degradation, through heat generation or phosphorescent radiation.
- The chromophore is excited by the light – attains a higher energy state from absorption of UV energy. Quencher is at lower energy state and "hijacks" the energy.
- Can stabilize regardless of the part thickness, so it can be used on films and fibers.
- Paramagnetic transition metal compounds are used, for example nickel phenolate.
- There are environmental concerns associated with heavy metals with these additives.

Hydroperoxide Decomposition

- Plastic formulation additives cause the breakdown of hydroperoxides, that are normally fundamental to the degradation reaction.
- Common types include metal complexes, and sulfur compounds, such as dialkyldithiocarbomates, dialkyldithiophosphates.
- Additives of this type are effective at low levels.
- Most commonly used in combination with UV absorbers.

Free Radical Scavenging

- These additives are similar to heat stabilizers used to protect against thermal decomposition. Realtionship of UV degradation and oxidation.
- Effectively “tie up” free radicals produced during the degradation reaction.
- Commonly used as part of a synergistic protective package. Not extremely effective as lone addives for photo-oxidation protection.
- Common type - phenolic compounds.

Hindered Amine Light Stabilizers

- These is the most important stabilizer type for many polymers.
- Protective mechanism is unclear.
- Proven that they do not absorb UV radiation or quench.
- Can be part of a synergistic package, comonly with phenolics.

Carbon Black

- Pigment and protective additive.
- Threshold of loading – commonly 2% in many polymeric materials.

Protection

Protection

Stabilizers typically react to the interaction of UV radiation and plastics by interrupting the degradation process

Another strategy is to protect the plastic from exposure to the UV radiation – UV Blocking.

Plastics can be coated to diminish the amount of ultraviolet radiation that passes through.

Protection

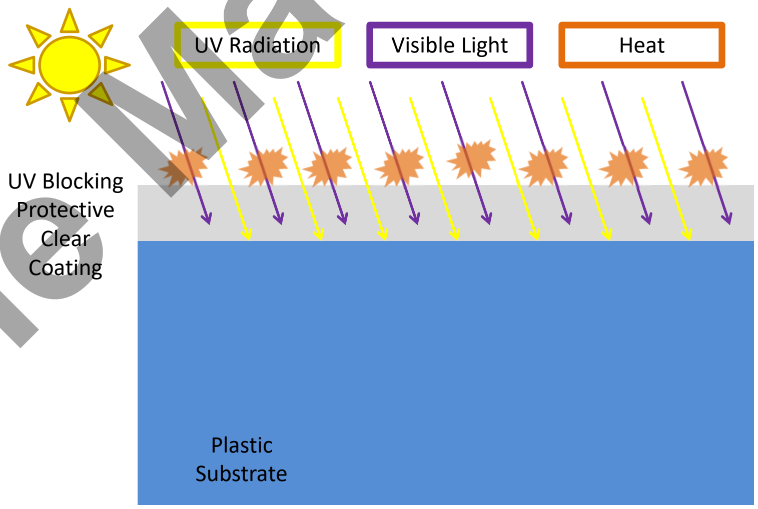
Coatings can provide a high level of protection for plastic components because they offer resistance to:

- UV radiation
- Weather
- Chemicals
- Dirt
- Scratches

Protection

- Paint: A substance that is composed of a solid coloring material applied as a protective or decorative layer to a substate.
- Clearcoat: A coating that is composed of a clear polymeric substance that is applied over the substrate to afford protection, yet maintain visibility of the substrate.

Protection



UV Radiation

Visible Light

Heat

UV Blocking
Protective
Clear
Coating

Plastic
Substrate

DETERMINING MOLECULAR DEGRADATION

Evaluating Degradation

Techniques

- Examination
- Indirect Analytical Methods
- Molecular Weight Assessment

Evaluating Degradation

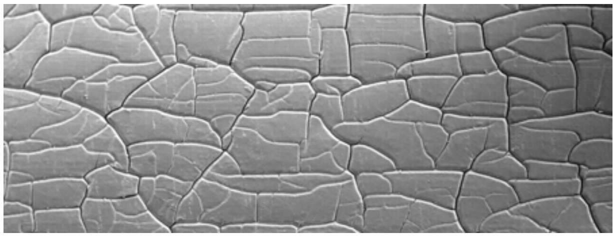
Examination Techniques

- Visual
- Microscopic
- Scanning electron microscopic (SEM)
- Cross section

Evaluating Degradation

Visual

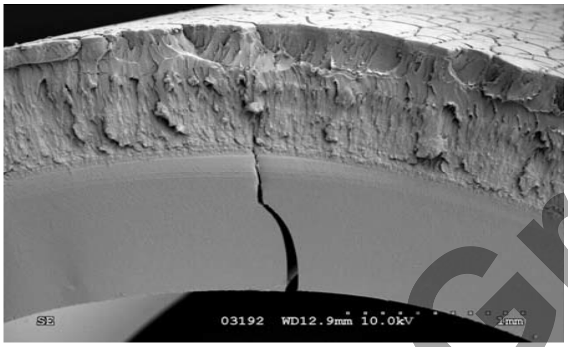
- Mud-cracked Appearance



Evaluating Degradation

Visual

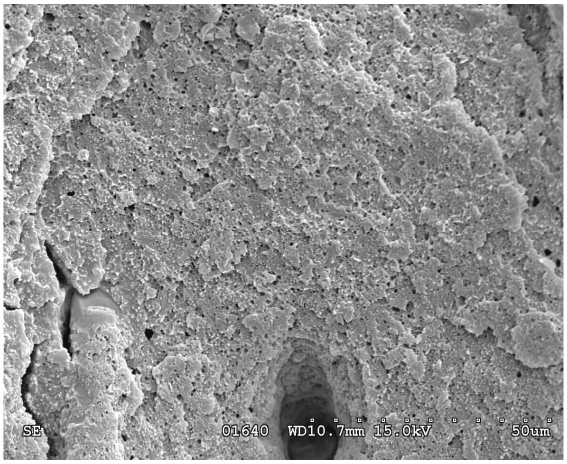
- Mud-cracked Appearance



Evaluating Degradation

SEM

- Coarse Fracture Surface Morphology
- Brittle Fracture
- Micro-porosity

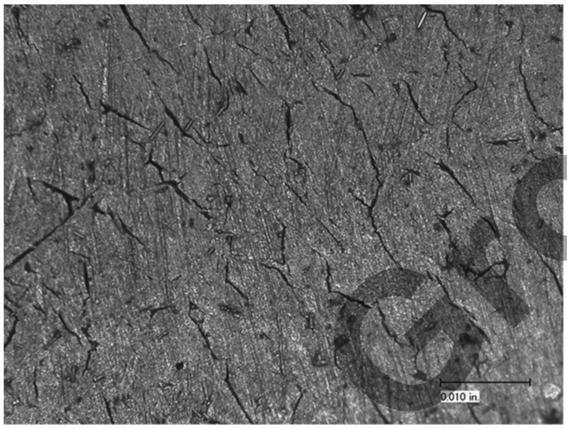


Permission to use granted by SPE. Ref: Jansen, Kosarzycki, and Sepe "Failure Analysis of Automotive Assemblies Parts I and II)" ANTEC 2002

Evaluating Degradation

SEM

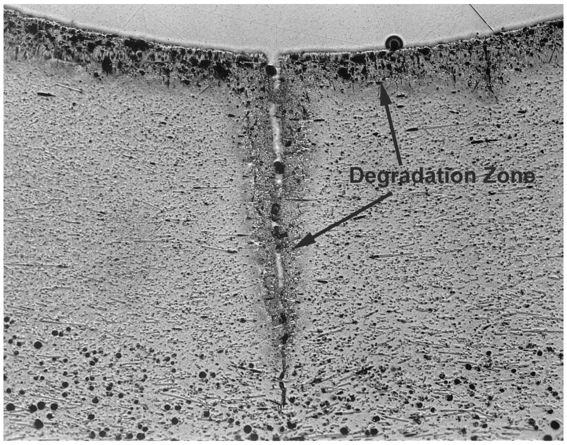
- Microscopic Surface Cracking
- Brittle Fracture



Evaluating Degradation

Cross Section

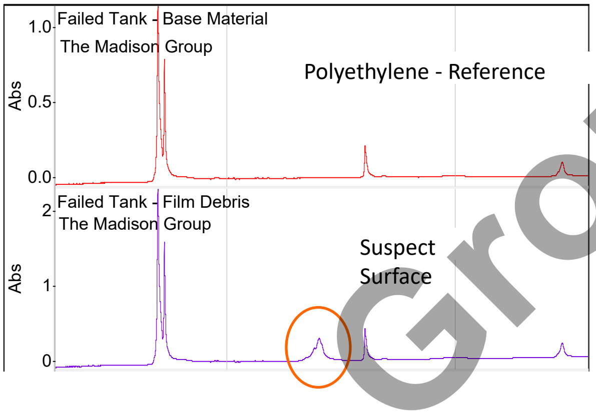
- Coarse Texture
- Darkened Color



Evaluating Degradation

FTIR

- Analysis of suspect surface material indicative of oxidized polyolefin
- Spectral bands ranging 1750 cm^{-1} to 1710 cm^{-1} - broad



Evaluating Degradation

Molecular Degradation is directly assessed through molecular weight determination

Three Key Methods:

- Gel Permeation Chromatography (GPC)
- Intrinsic Viscosity (IV)
- Melt Flow Rate (MFR)

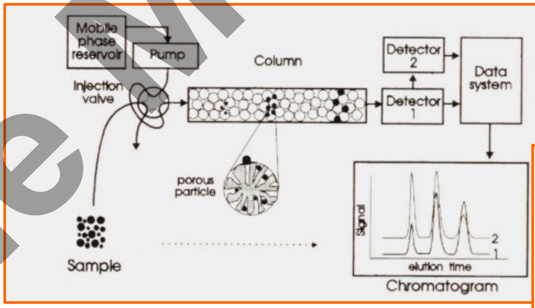
Evaluating Degradation

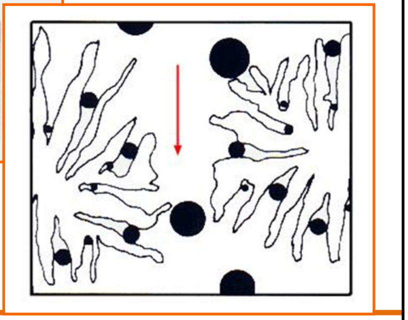
Gel Permeation Chromatography (GPC)

- GPC is a type of size exclusion chromatography based on liquid chromatography
- Separates analytes on the basis of size - smaller molecules are retained in the packed column
- Plastic sample is dissolved in an appropriate solvent
- Various detectors including: infrared absorption, light scattering, differential refractive index, ultraviolet absorption
- Produces a "bell-shaped" distribution of molecular weight

Evaluating Degradation

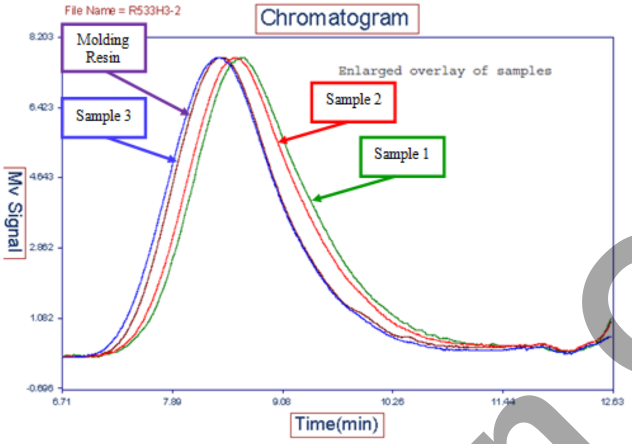
Gel Permeation Chromatography (GPC)





Evaluating Degradation

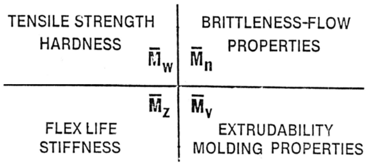
Gel Permeation Chromatography (GPC)



Evaluating Degradation

Gel Permeation Chromatography Results
(Average Molecular Weight)

Sample	Run	M_n		M_w		M_z		M_w/M_n	
Molding Resin	1	9,702	9,759	46,512	46,556	84,961	85,207	4.79	4.77
	2	9,816		46,601		85,093		4.75	
Sample 1	1	9,003	9,085	33,926	33,881	64,318	64,261	3.77	3.73
	2	9,167		33,835		64,204		3.69	
Sample 2	1	8,416	8,443	37,439	37,407	71,367	71,136	4.45	4.43
	2	8,470		37,375		70,905		4.41	



TENSILE STRENGTH
HARDNESS
$\bar{M}_w$

$\bar{M}_n$
BRITTLENESS-FLOW
PROPERTIES

FLEX LIFE
STIFFNESS
$\bar{M}_z$

$\bar{M}_v$
EXTRUDABILITY
MOLDING PROPERTIES

Reduction in molecular weight from degradation

Evaluating Degradation

Intrinsic Viscosity

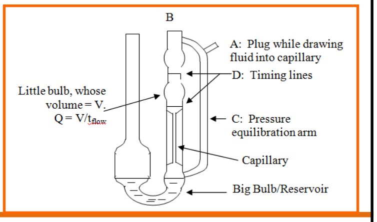
- IV is a measure of the capability of a polymer in solution to enhance the viscosity of the solution
- Indirect measurement of the average molecular weight:

↑ Average Molecular Weight - ↑ IV

Evaluating Degradation

Intrinsic Viscosity

- ASTM D 2857
- The polymer is dissolved in an appropriate solvent
- Sample size: 40-50 mg
- Measure the flow time of a solution through a glass capillary – Ubbelohde viscometer
- Testing is conducted to find the viscosity at different concentrations and then extrapolate to zero concentration



Evaluating Degradation

Melt Flow Rate / Melt Viscosity

- Most common measure of molecular weight
- Test method: ASTM D 1238
- Measures the flow of a thermoplastic material through a specified orifice under unique conditions of temperature and load
- Units: g/10 min.

Evaluating Degradation

Melt Flow Rate / Melt Viscosity

- *MFR is an indirect measure of average molecular weight*
- MFR is inversely proportional to the average molecular weight:

↑ Average Molecular Weight – ↑ Melt Viscosity – ↓ Melt Flow Rate

- MFR testing does not generate a direct measure of the average molecular weight, however:

$$MFR \approx M_w^{3.4}$$

$$M_w \approx MFR^{0.238}$$

- The standard MFR test does not provide information regarding the molecular weight distribution
- Experiments can be run to assess thermal stability

Failure Cases

Photo Oxidation - Performance

Critical Parameters

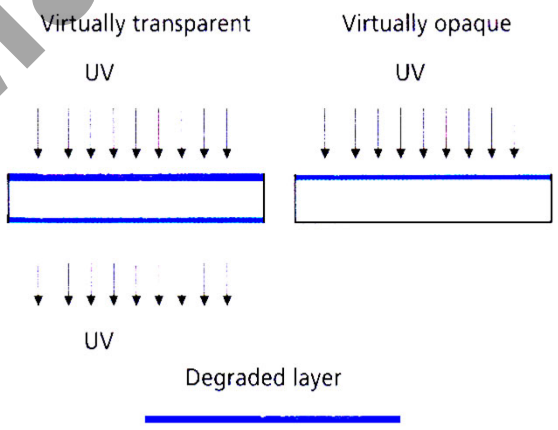
- Severity of exposure
- Polymer type
- Formulation additives - nonprotective
- Contaminants
- Quality and quantity of stabilization package

Photo-oxidation Failures

Hidden Surface

- Significant degradation can occur at “hidden” surfaces that are not exposed to UV radiation.
- When products are subjected to combined UV exposure and bending stress, with “hidden” surface under tensile stress and external surfaces under compression, cracking will tend to initiate at the “hidden” surface.

Photo-oxidation Failures



Virtually transparent

UV

UV

Virtually opaque

UV

Degraded layer

Water Supply Tubing

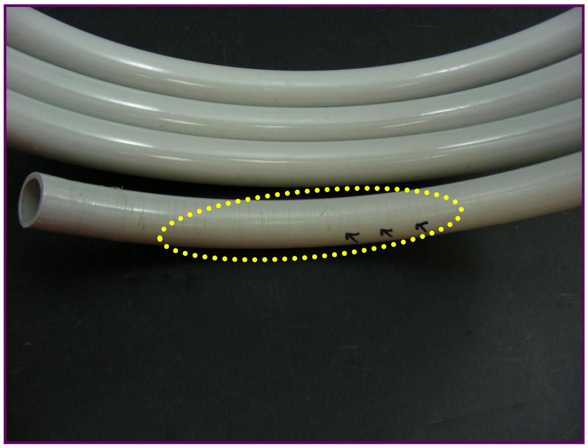
Background

- Thermoplastic polyester water supply tubing.
- Failed while in service in an uncovered pit – water leakage.
- Failure after approx. 8 months in service.

Water Supply Tubing

Visual

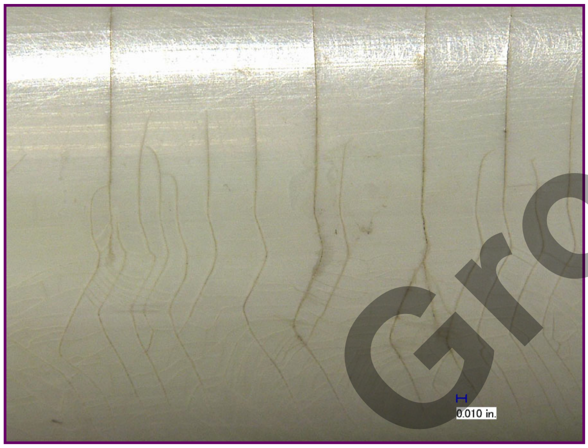
- Cracking present on one end of the tubing near mating brass fitting.
- Cracking initiated approximately 1½ in. from the end of the fitting and extended approximately 12 in.



Water Supply Tubing

Visual

- Cracking present as a series of transverse cracks located exclusively on the inner diameter of the tubing as it was coiled.
- Transverse cracks - axial loads.
- No signs of macro-ductility.
- Macro features characteristic of brittle fracture.



Water Supply Tubing

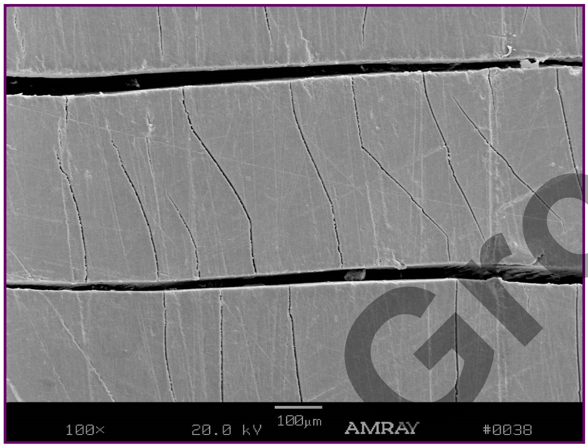
Visual

- Distinct discoloration was evident within the general area of cracking.

Water Supply Tubing

SEM

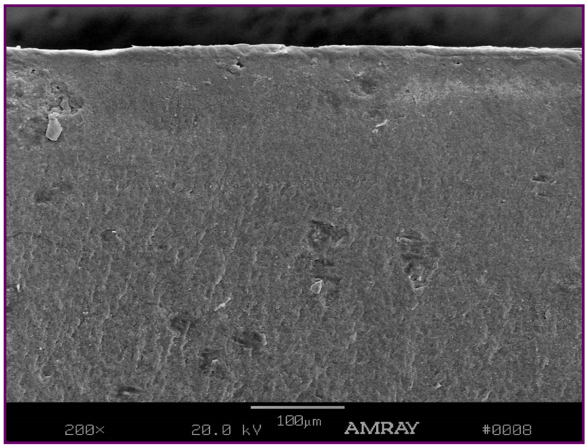
- At high magnification, intersecting cracks oriented longitudinally were also apparent.
- No micro-ductility.
- Crack pattern consistent with molecular degradation of the tubing material.



Water Supply Tubing

SEM

- Fracture surface showed crack origin at exterior surface of tubing.
- Smooth morphology – brittle fracture / slow crack growth mechanism.



Water Supply Tubing

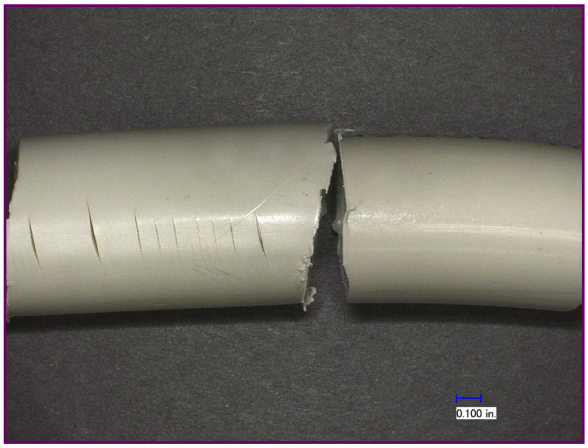
Cross Section

- Parallel cracking consistent with the exterior observations.
- No signs of bridging or ductility.
- General shape of the cracking consistent with initiation along the exterior surface of the tubing wall.
- No evidence to indicate production defects or anomalies within the extruded tubing.

Water Supply Tubing

Mechanical Testing

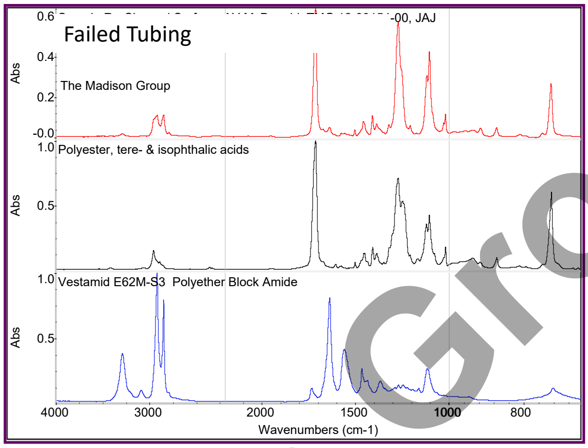
- Flattening test conducted on tubing samples - specimens extracted from the failure zone and non-failed end.
- Results indicated that the material within the failure zone was in a compromised state, predisposed to cracking.
- No cracking in non-failed end.



Water Supply Tubing

FTIR

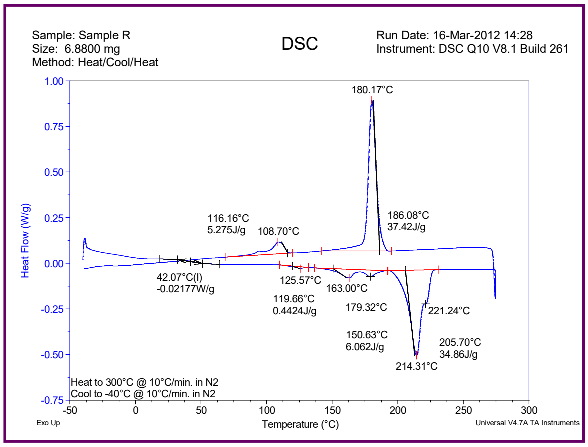
- FTIR results characteristic thermoplastic polyester with a polyether block amide.



Water Supply Tubing

DSC

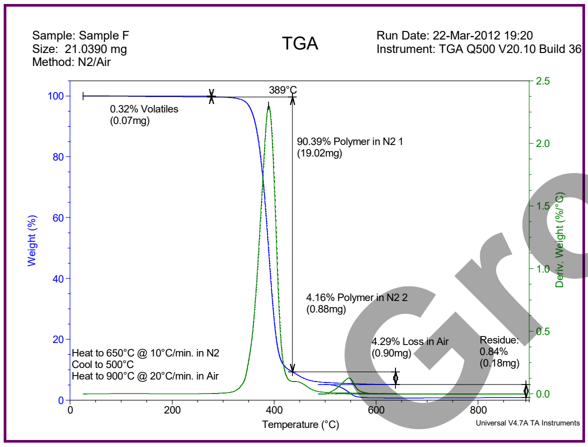
- DSC indicated a primary endotherm at 214 °C - melting transition of poly(butylene terephthalate) (PBT) the base thermoplastic polyester.
- Weaker bimodal endotherm, with individual maxima at 163 °C and 179 °C - associated with the melting of the amide-based polymer.



Water Supply Tubing

TGA

- TGA showed failed and reference materials exhibited extremely similar weight loss profiles.
- Separate transitions represented the poly(butylene terephthalate) (PBT) and polyether block amide constituents.
- No evidence of contamination or bulk molecular degradation was found.



131

Water Supply Tubing

MFR

- MFR results showed that failed tubing material had an average molecular weight similar to new unused tubing material.
- Not suggestive of bulk molecular weight changes or molecular degradation of the failed tubing material.

Melt Flow Rate Test Results

(g/10 min.)

Test	Sample R	Sample F
1	32.74	32.28
2	33.62	32.89
3	34.22	34.60
4	35.27	35.62
5	36.31	37.22
6	36.80	38.12
Average	34.83	35.12

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Water Supply Tubing

Conclusions - Failure Mechanism

- Tubing failed via brittle fracture through a slow crack initiation and growth mechanism.
- The failure was associated with significant molecular degradation of the exterior surface of the tubing within a limited area.
- The mechanical stresses responsible for the cracking are thought to be associated with tensile loads created during bending of the tubing against the coiled direction. Such bending would place the inner diameter of the coil in tension.

Water Supply Tubing

Conclusions - Cause

- Molecular degradation is thought to be associated with ultraviolet (UV) radiation through exposure to sunlight. The open nature of the pit could result in exposure to sunlight. The extreme surface isolation of the degradation and the relatively limited area over which the cracking occurred precluded thermal degradation.
- No evidence of contaminant chemical agents was found.
- No signs of defects or production anomalies were found in the tubing samples.

Equipment Housing

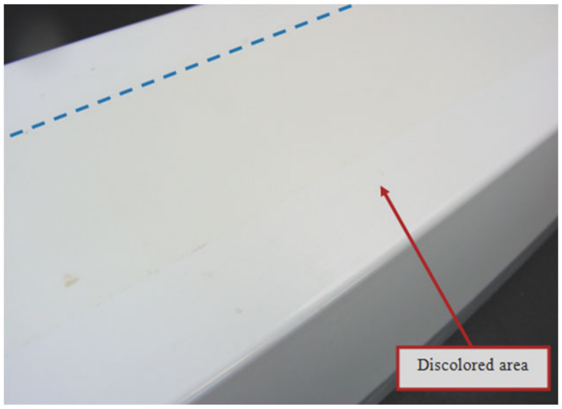
Background

- The housing for a piece of electrical equipment used in an office application discolored after a relatively short period of time.
- Failure at a number of installations.
- No outdoor exposure – minimal indirect sunlight.
- Injection molded from impact modified polystyrene (HIPS)

Equipment Housing

Visual

- Visually a yellow discoloration was evident on the surface of the housings.
- Discoloration limited to "exposed" areas. Covered areas were not discolored.



Equipment Housing

Visual

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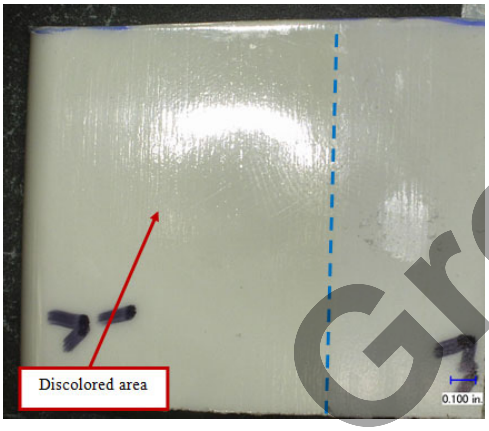
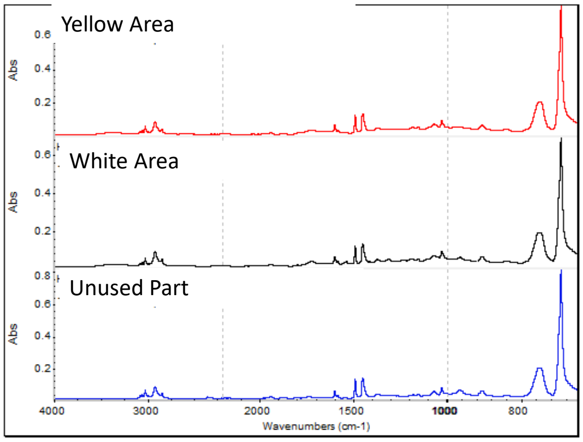


Equipment Housing

FTIR

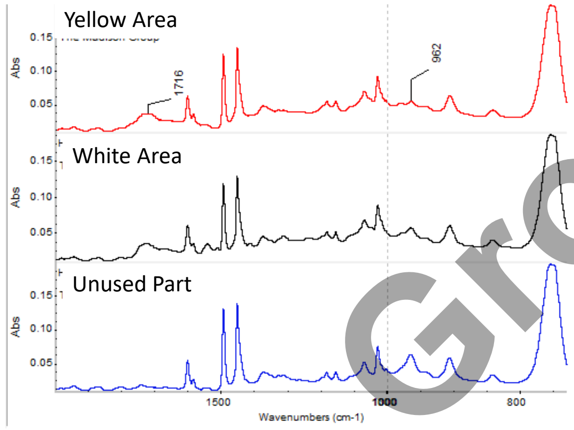
- Both discolored and non-discolored areas produced spectra characteristic of HIPS.



Equipment Housing

FTIR

- Reduction in butadiene absorption band
- Corresponding increase in carbonyl band.



Conclusions

- Discoloration of the housing was associated with UV exposure form office fluorescent lighting.
- Thought that minimal/no UV stabilization package was present in material.

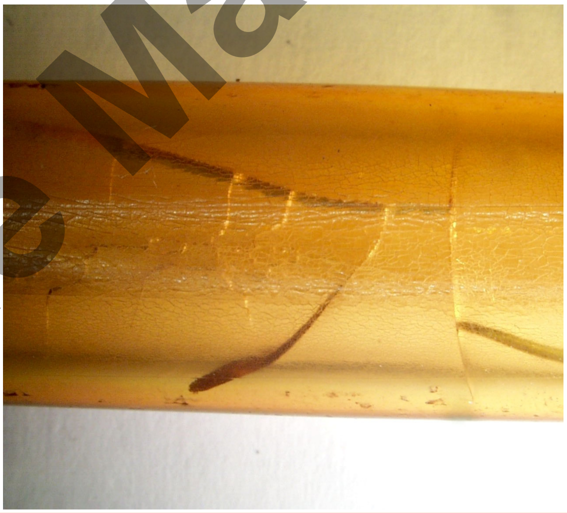
Fuel Line Failure

Background

- Fuel Line
- Cracking Occurred While in Service
- Approximately 2 Years in the Field
- Fuel Leakage
- Poly(ether urethane) Resin

Previously Published/Presented at IATC-2003

Fuel Line Failure



Visual

- Significant level of cracking
- Cracking limited to areas which had been exposed in the application
- Intersecting network of cracks

Previously Published/Presented at IATC-2003

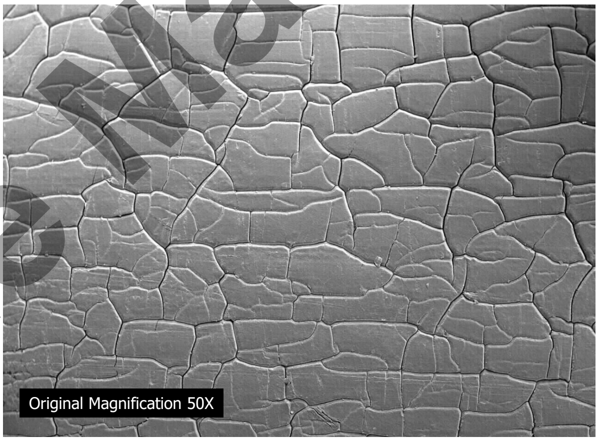
Fuel Line Failure

Visual

- Crack network more prevalent on OD surface

Previously Published/Presented at IATC-2003

Fuel Line Failure

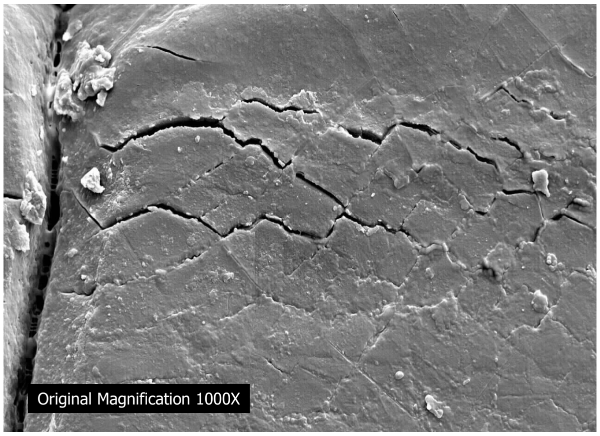


SEM

- OD surface showed network of perpendicular cracks
- Characteristic of molecular degradation

Previously Published/Presented at IATC-2003

Fuel Line Failure



SEM

- Micro cracking
- Relatively smooth surface texture

Previously Published/Presented at IATC-2003

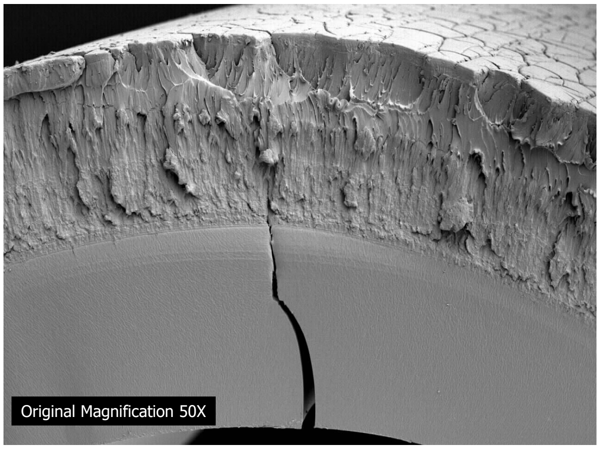
Fuel Line Failure

SEM

- ID surface - very smooth
- Fewer cracks
- Network of perpendicular cracking
- Smooth surface texture

Previously Published/Presented at IATC-2003

Fuel Line Failure

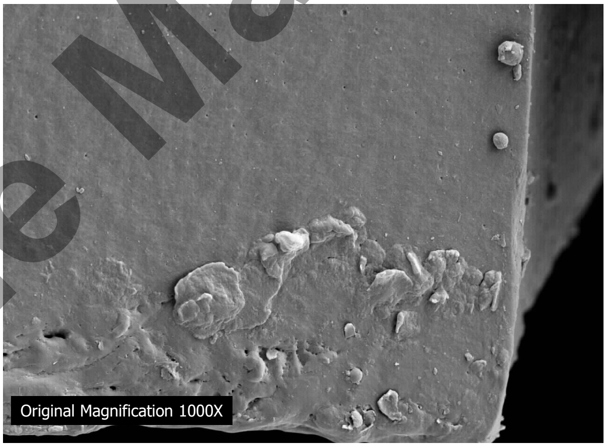


SEM

- Crack origin location along ID edge
- Smooth fracture surface
- Secondary cracking
- Coarse texture along OD - Final fracture zone via overload

Previously Published/Presented at IATC-2003

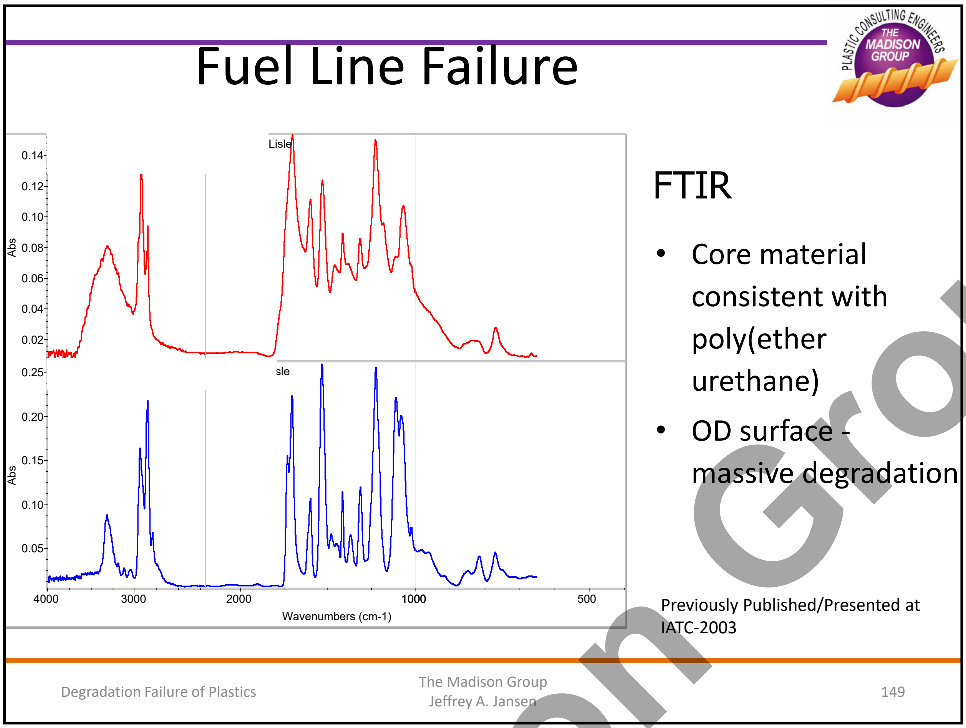
Fuel Line Failure



SEM

- Crack origin location along ID edge
- Smooth fracture surface

Previously Published/Presented at IATC-2003



Fuel Line Failure

FTIR

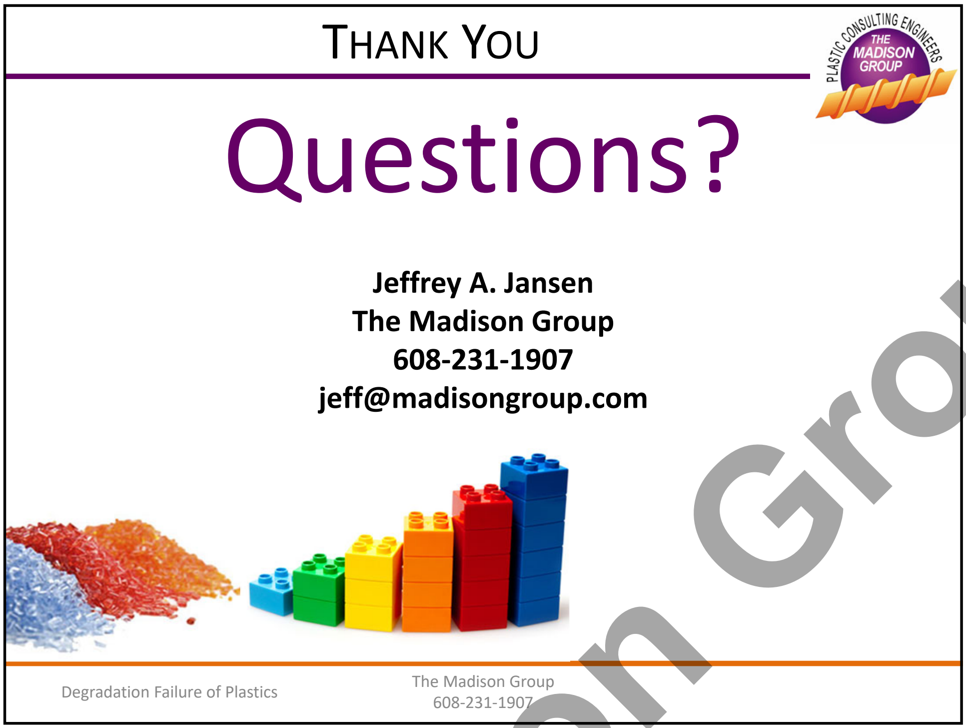
- Core material consistent with poly(ether urethane)
- OD surface - massive degradation

Previously Published/Presented at IATC-2003

Conclusions

- Fuel line failed via brittle fracture. Cracking initiated due to molecular degradation associated with UV exposure. Gasoline effected degraded material to extend cracks from defects.

Previously Published/Presented at IATC-2003



THANK YOU

Questions?

Jeffrey A. Jansen
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Degradation Failure of Plastics

The Madison Group
608-231-1907

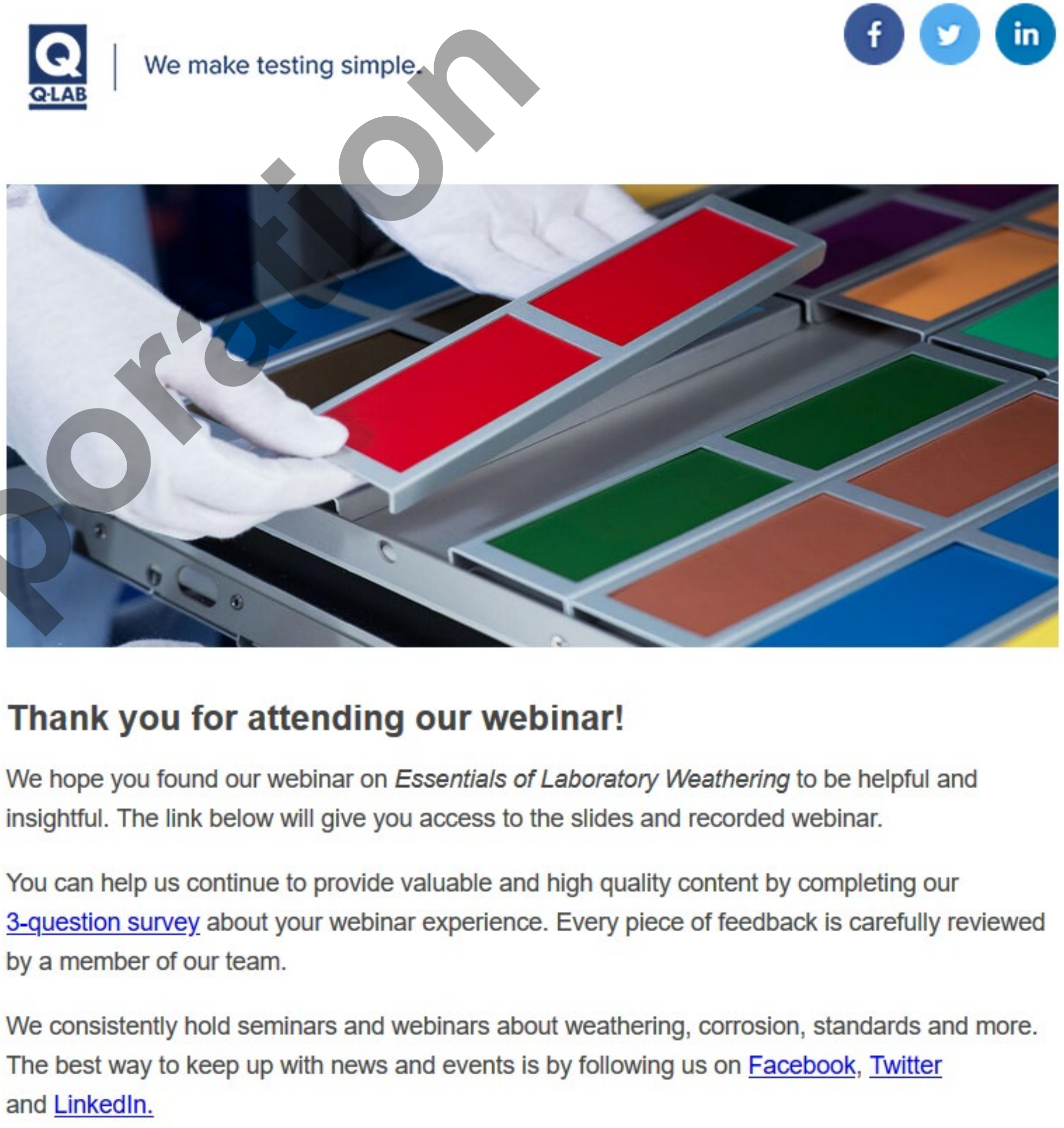
Laboratory Weathering Testing of Plastics

Q-Lab Corporation

Reminders

You'll receive a follow-up email from info@email.q-lab.com with links to a survey, registration for future webinars, and to download the slides

- Our ongoing webinar series can be found at: q-lab.com/webinarseries
- Our archived webinars are hosted at: q-lab.com/webinars
- Q&A feature in Zoom is open for questions during this part



Thank you for attending our webinar!

We hope you found our webinar on *Essentials of Laboratory Weathering* to be helpful and insightful. The link below will give you access to the slides and recorded webinar.

You can help us continue to provide valuable and high quality content by completing our 3-question survey about your webinar experience. Every piece of feedback is carefully reviewed by a member of our team.

We consistently hold seminars and webinars about weathering, corrosion, standards and more. The best way to keep up with news and events is by following us on Facebook, Twitter and LinkedIn.

Laboratory Weathering Testing

- **Basics of Weathering**
- Why Perform Laboratory Weathering Testing?
- Lab Weathering Test Instruments
  - Xenon
  - Fluorescent UV
- Elements of an Effective Testing Program

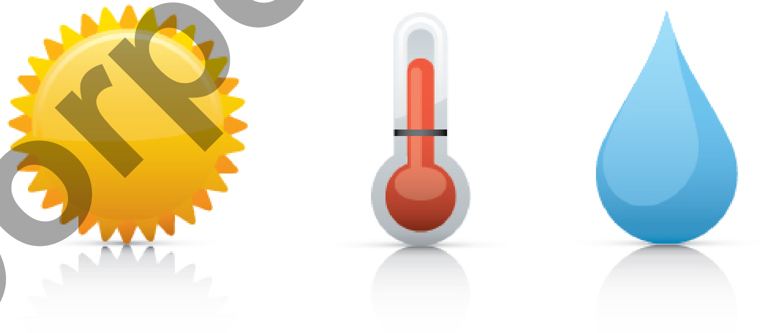
What is Weathering?

Changes in material properties resulting from exposure to the radiant energy present in **sunlight** in combination with **heat** (including temperature cycling) and **water** in its various states, predominately as humidity, dew, and rain.

Forces of Weathering

Primary Causes of Polymer Degradation

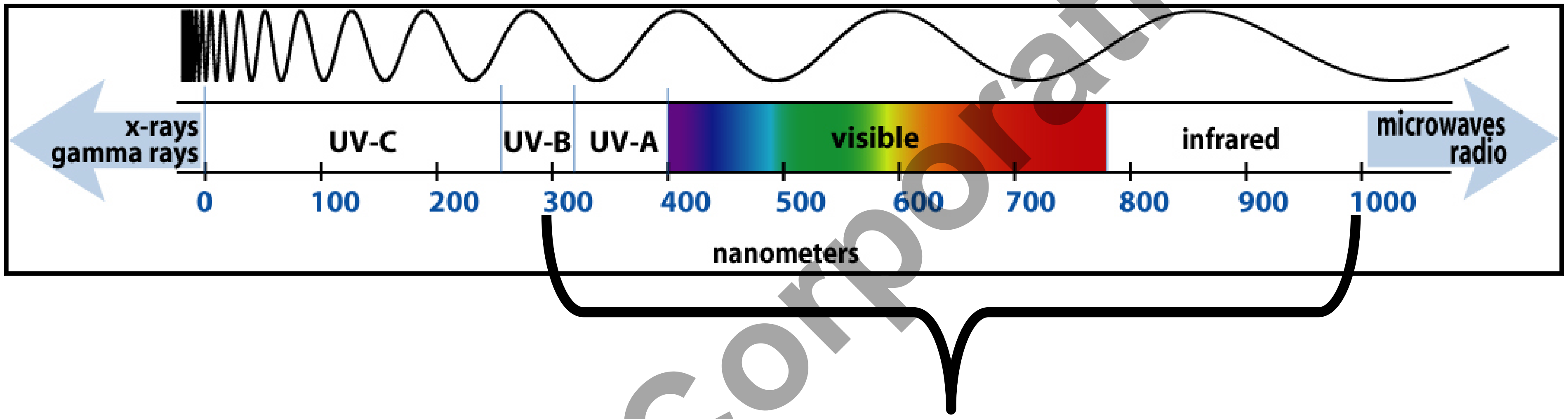
- Sunlight
- Heat
- Water



**Other factors can impact weathering as well but we will not focus on those today*

Sunlight

Electromagnetic Spectrum

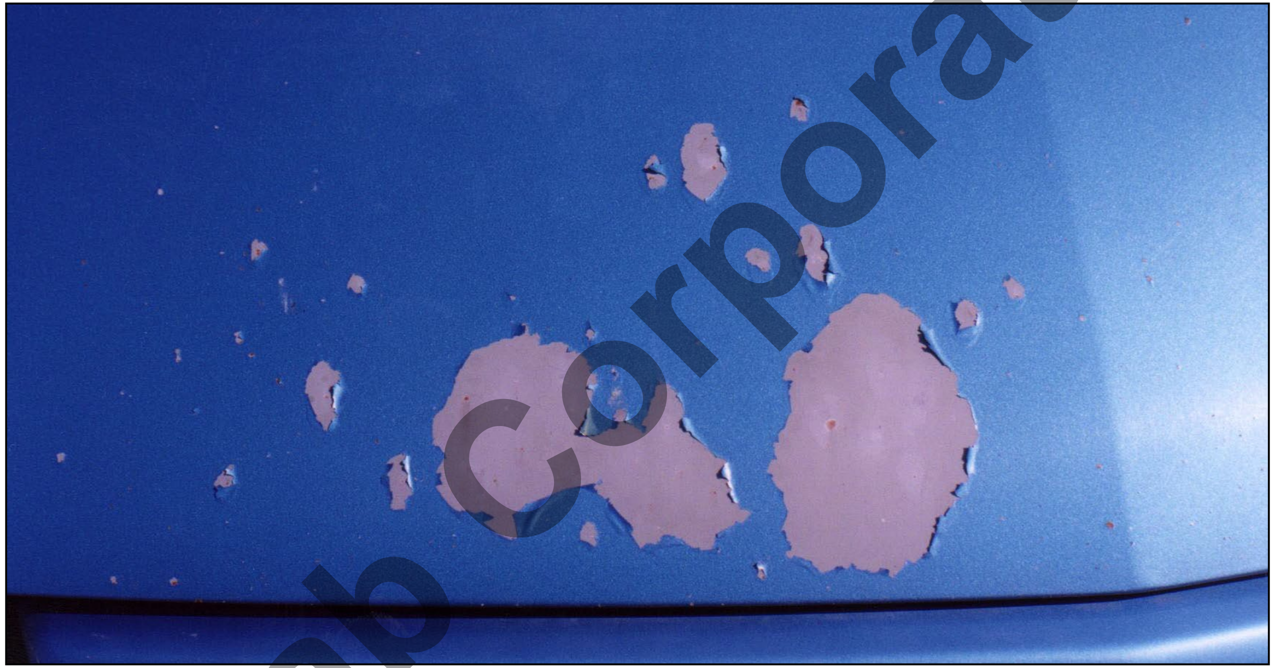


- A form of energy
- Electromagnetic radiation
- Usually described in terms of **irradiance** & **wavelength (λ)**

Sunlight

UV	**295-400 nm**	**~7%**
Visible	400-800 nm	~55%
IR	800-3000 nm	~38%

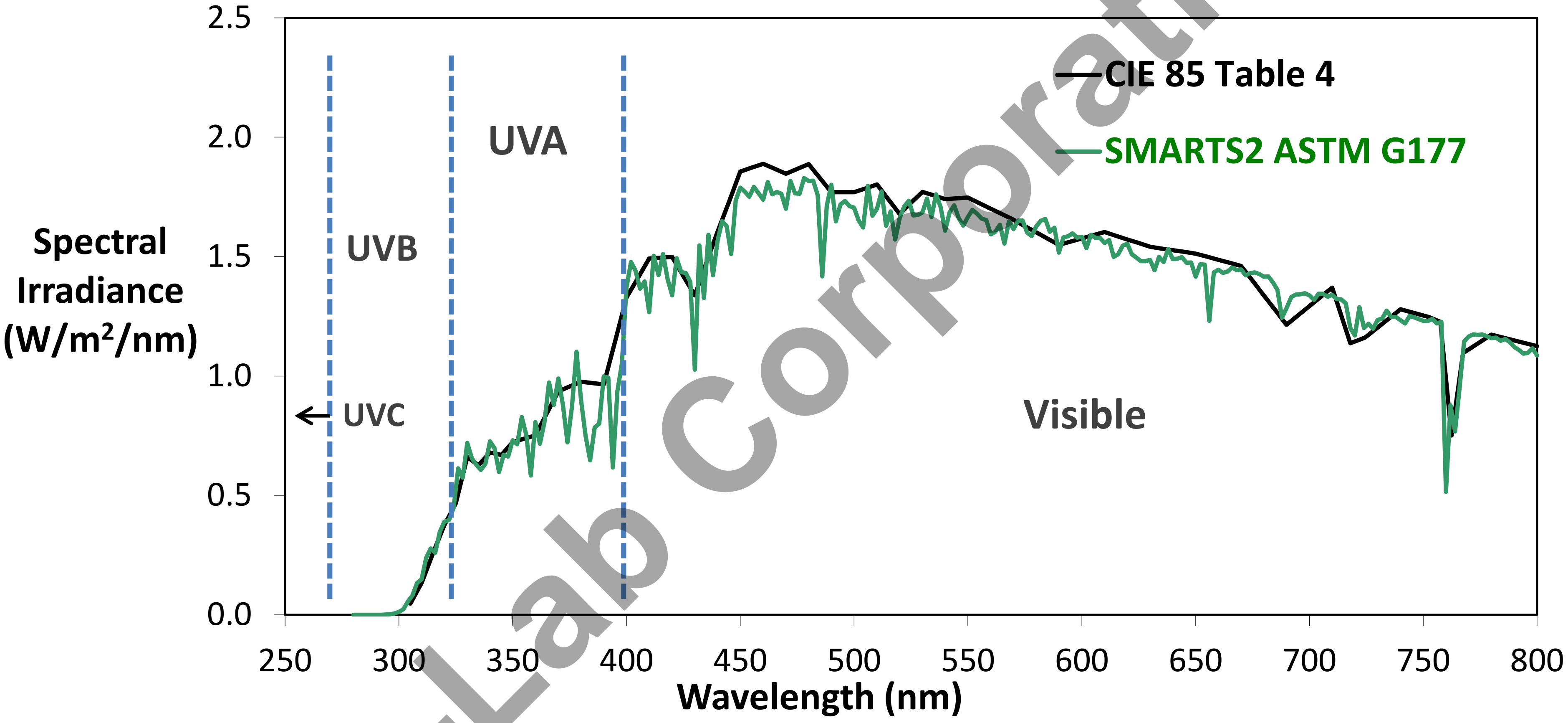
Even though it is only 7% of sunlight's total radiant energy...



UV causes virtually all polymer degradation!

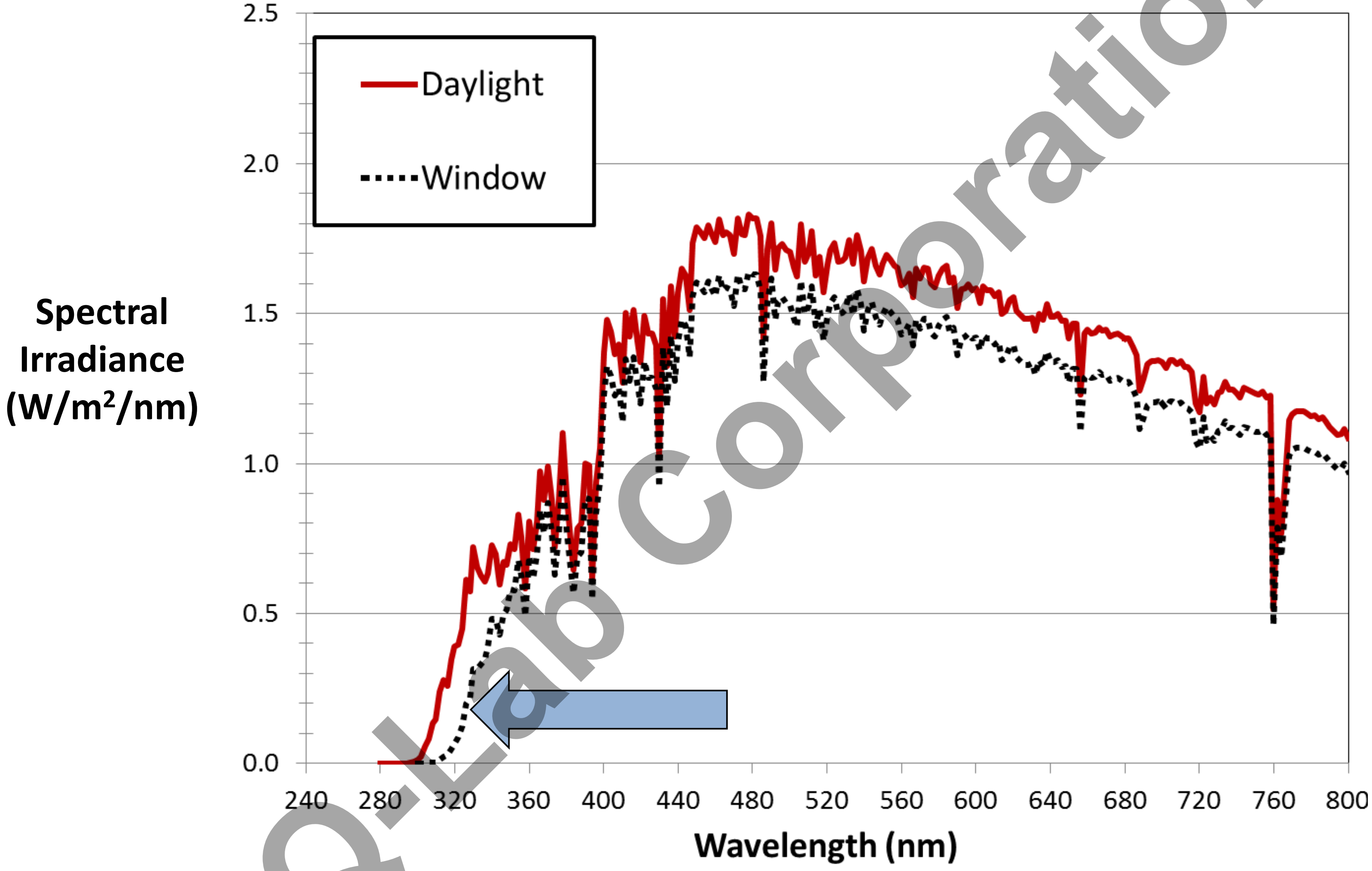
Spectral Irradiance

(Spectral Power Distribution, SPD)

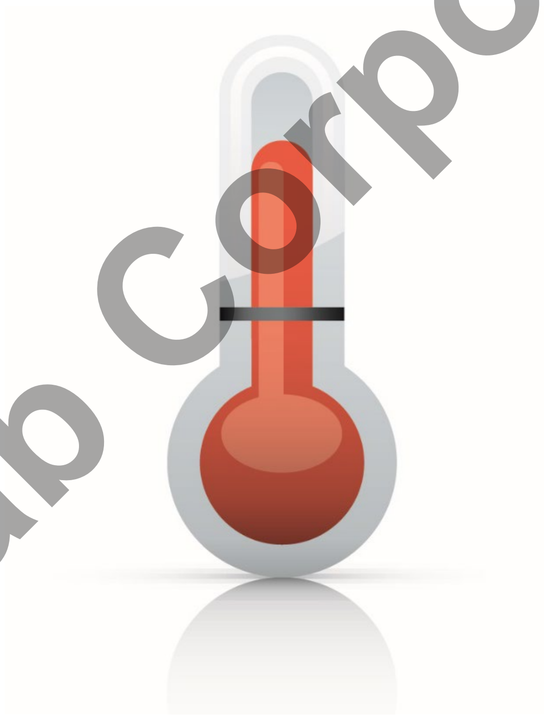


SPD: The absolute or relative radiant power emitted by a source, or incident upon a receiver as a function of wavelength. (ASTM G113)

Sunlight Through Window Glass



Heat

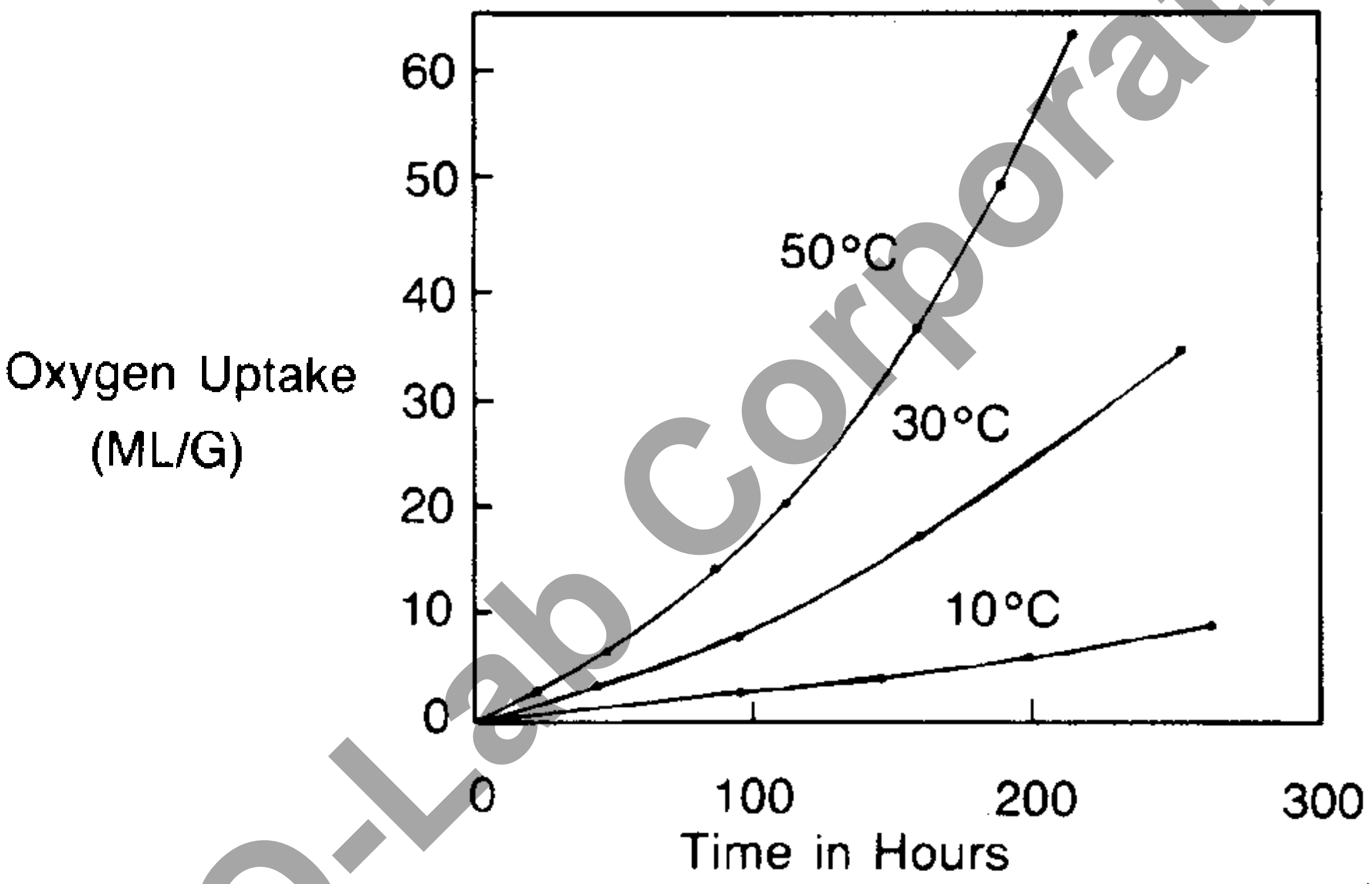


Heat Effects

- Elevated specimen temperature
- Dimensional change
- Evaporation
- Thermal aging
- Thermal cycling

Effect of Temperature:

Oxidation Rate of Polyethylene



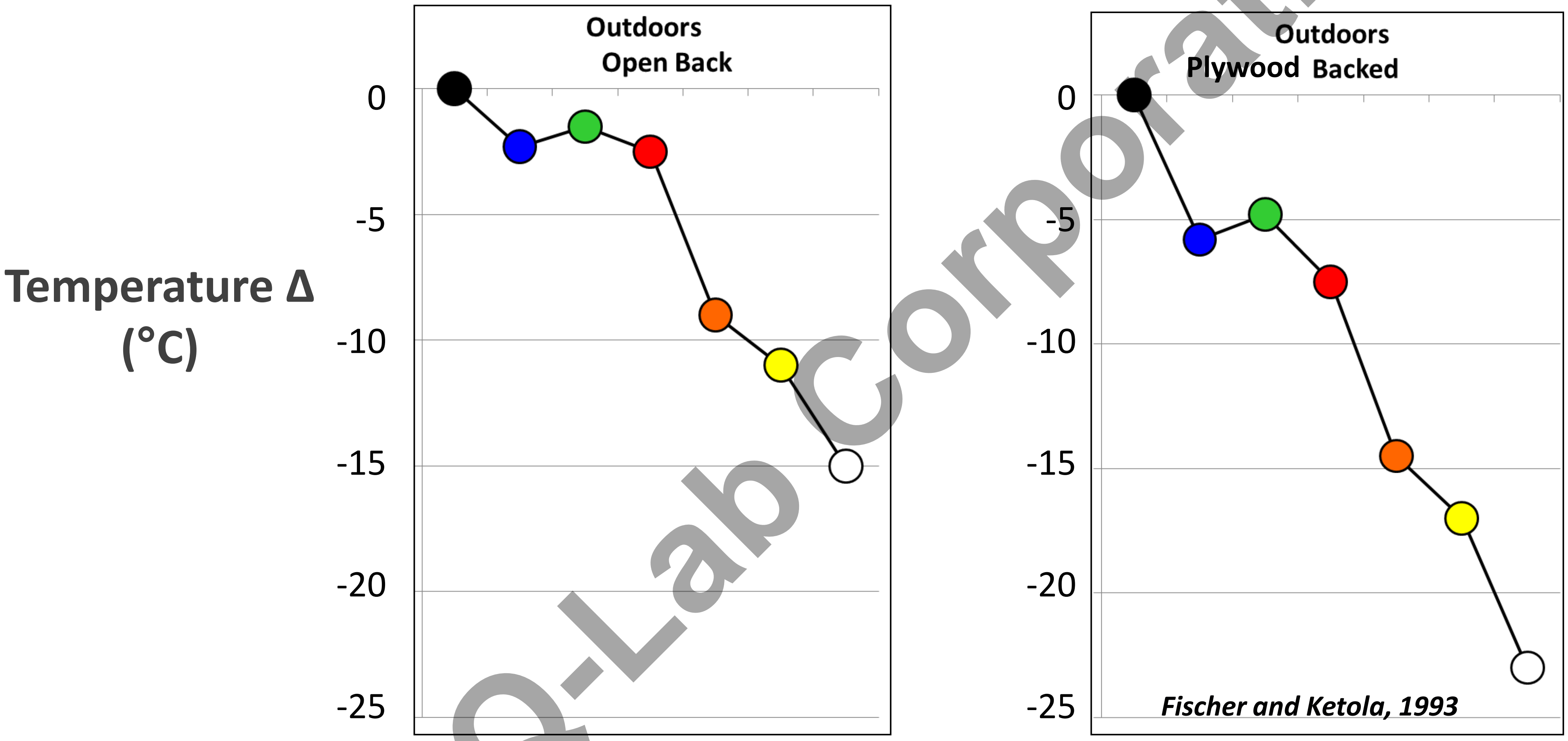
*Time In Hours Exposed to UV lamps

Thermal Cycling in Florida

- 75 °C to 25 °C in 2 minutes
- Causes physical stress
- Affects coatings on plastics and assemblies

Temperature and Color

Darker Colors Have Higher Temperatures!

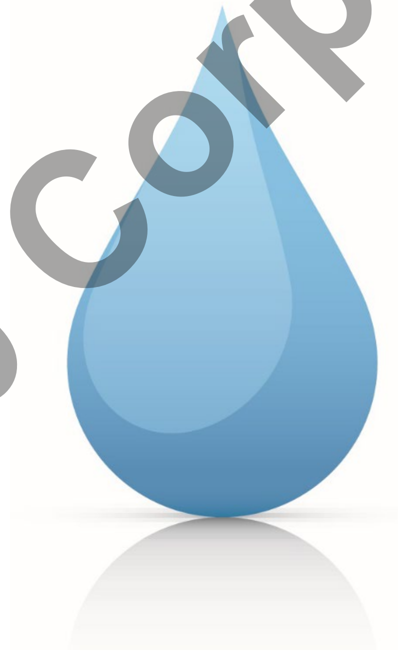


Fischer and Ketola, 1993

Heat behind Window Glass

Temperature of automobile interior components behind window glass can exceed 100 °C

Water



Major Effects of Water

Chemical Reactions

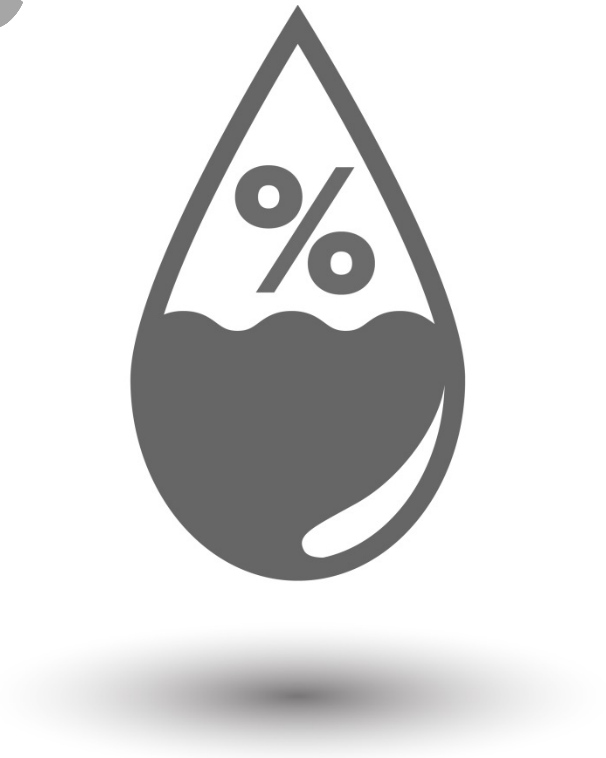
- Reactions in solution
- Facilitates reaction via increase in oxygen transport

Physical Effects

- Erosion
- Absorption/freeze-thaw
- Thermal shock
- Impact (material loss)

Humidity

- **Measure of amount of water in air**
- Can lead to physical stress
- Humidity affects products both indoors and outdoors
- Often expressed as Relative Humidity (RH), where 100% is the most water that air of a given temperature can hold



Rainfall

- Surface effects
  - Washing away surface layers
  - Chalking
  - Dirt removal

- Thermal shock

Dew

- Moisture from the atmosphere that forms in the form of small drops upon any cool surface
- High O_2 and long dwell time
- Dew, not Rain, is the source of most outdoor wetness!

Dew Is Not Simulated in Many Accelerated Lab Weathering Tests!

Don’t Underestimate the Effect of Moisture!

- Changes the **rate** of degradation
- Changes **mode** of degradation
- Difficult to **accelerate**

Summary: Forces of Weathering

Sunlight

- UV light causes virtually all polymer degradation
- Small changes in material formulation and/or spectrum can have large effects on material degradation

Heat *(Temperature)*

- Sunlight + Heat = increased rate of degradation
- A material's color strongly affects how hot it will get in sunlight

Water *(Moisture)*

- Sunlight + Heat + Water = Weathering
- Dew, not Rainfall, is the source of most outdoor wetness
- Products outdoors are wet much longer than you think

Weathering includes synergistic effects between these factors!

Laboratory Weathering Testing

- Basics of Weathering
- **Why Perform Laboratory Weathering Testing?**
- Lab Weathering Test Instruments
  - Xenon
  - Fluorescent UV
- Elements of an Effective Testing Program

Why Test?

- Meet specifications
- Avoid catastrophes
- Enhance your reputation
- Verify supplier claims
- Improve product durability

- Save on material costs
- Expand existing product lines
- Enter new markets
- Outrun the competition
- Stay ahead of regulations

Laboratory Testing is a Tool for **Directional Decision-Making**

Laboratory Accelerated tests can help you:

- Make decisions better and/or faster
- Reduce risk of making bad decisions
- Reduce risk of making decisions too slowly

What Kind of Test Should I Run?

Accelerated Test Type	**Result**	**Test Time**	**Results compared to**
Quality Control	Pass / fail	• Defined • Short	Material specification

What Kind of Test Should I Run?

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Correlative	Rank-ordered data	• Open-ended • Medium	Natural exposure (Benchmark site)

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Predictive	Service life Acceleration factor	• Open-ended • Long	Natural exposure (Service environment)

What Kind of Test Should I Run?

Accelerated Test Type	**Result**	**Test Time**	**Results compared to**
Quality Control	Pass / fail	• Defined • Short	Material specification
Qualification / validation	Pass / fail	• Defined • Medium-long	Reference material or specification
Correlative	Rank-ordered data	• Open-ended • Medium	Natural exposure (Benchmark site)
Predictive	*Service life* *Acceleration factor*	• *Open-ended* • *Long*	*Natural exposure (Service environment)*

What is **Natural** Weathering?

Outdoor exposure of materials to unconcentrated sunlight, the purpose of which is to assess the effects of environmental factors on various functional and decorative parameters of interest.

Global benchmark weathering sites:

- South Florida (Subtropical)
- Arizona (Dry Desert)
- Midwest (Northern Industrial)

Why Is Natural Weathering Important?

- Natural weathering is more complex than artificial (laboratory) weathering
- Accelerated laboratory tests are not always realistic
- Laboratory test accuracy should always be verified by outdoor tests
- Ongoing outdoor weathering tests build a library of highly valuable data, at low cost

Laboratory Weathering Testing

- Basics of Weathering
- Why Perform Laboratory Weathering Testing?
- **Lab Weathering Test Instruments**
  - **Xenon**
  - **Fluorescent UV**
- Elements of an Effective Testing Program

Xenon Arc

Laboratory Weathering Testing

Xenon Arc Test Chamber: Flat Array

1) Simple user interface
2) USB port for data transfer
3) Xenon lamps with irradiance control
4) Optical filters
5) Water spray
6) Onboard irradiance sensors
7) Black Panel Temp sensor
8) Specimen holders
9) Relative Humidity/CAT sensor

Xenon Arc Test Chamber: Rotating Rack

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6) Onboard irradiance sensors
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9) Relative Humidity/CAT sensor

Xenon Arc Lamps


Air-cooled


Water-cooled

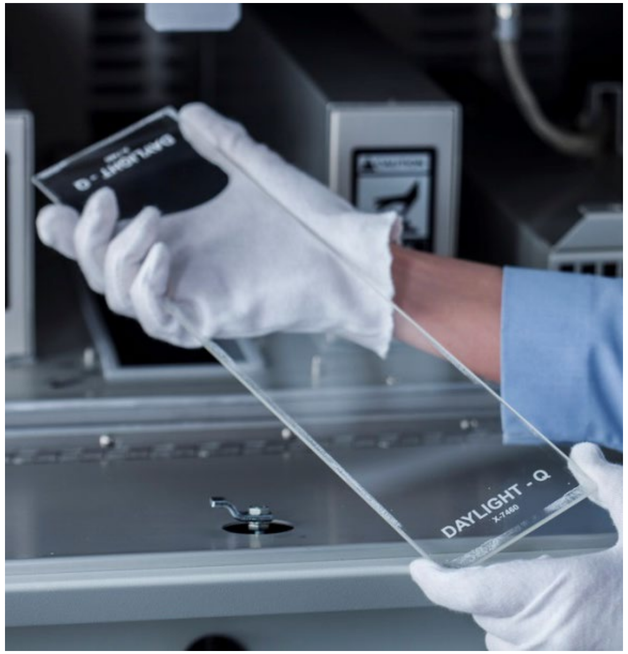
Water-cooled Assembly

Optical Filters

- Daylight
- Window
- Extended UV

Rotating drum "lantern"

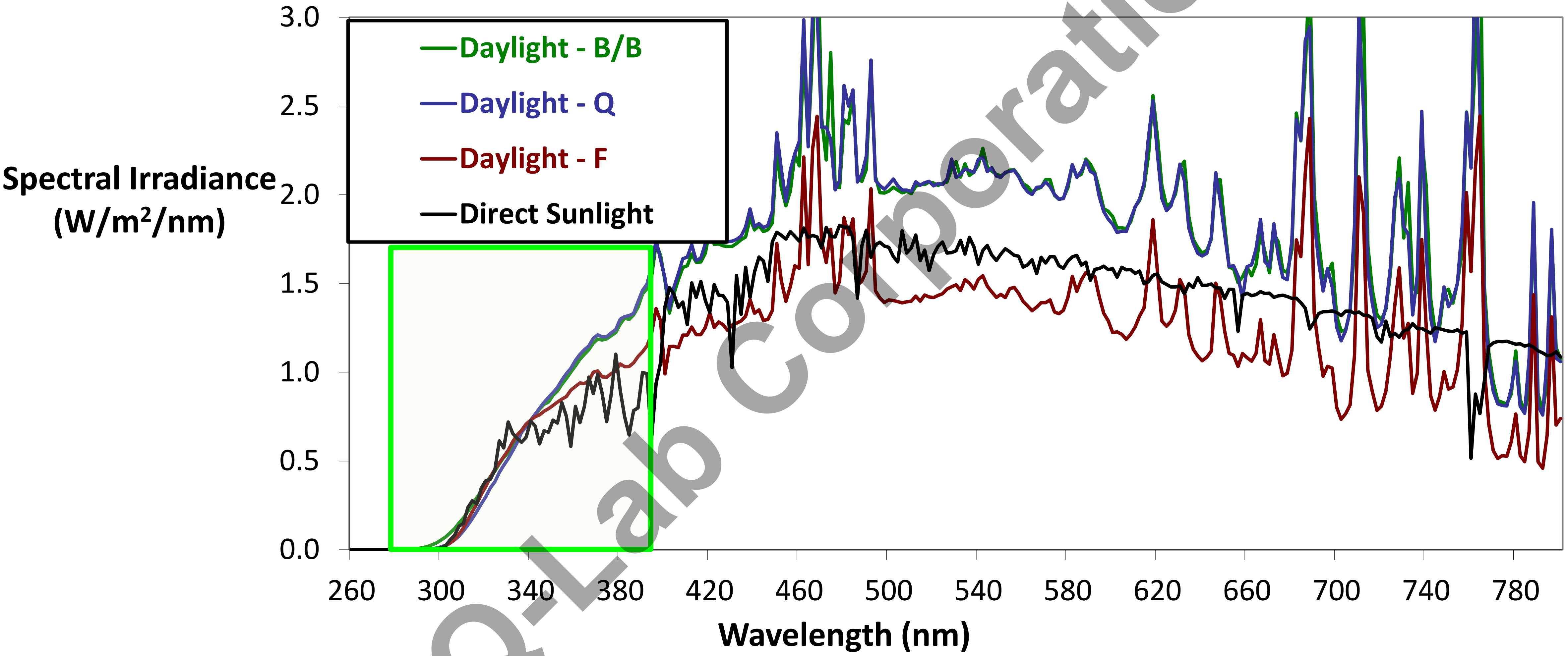
Flat array filter



**Other specialized filters used occasionally*

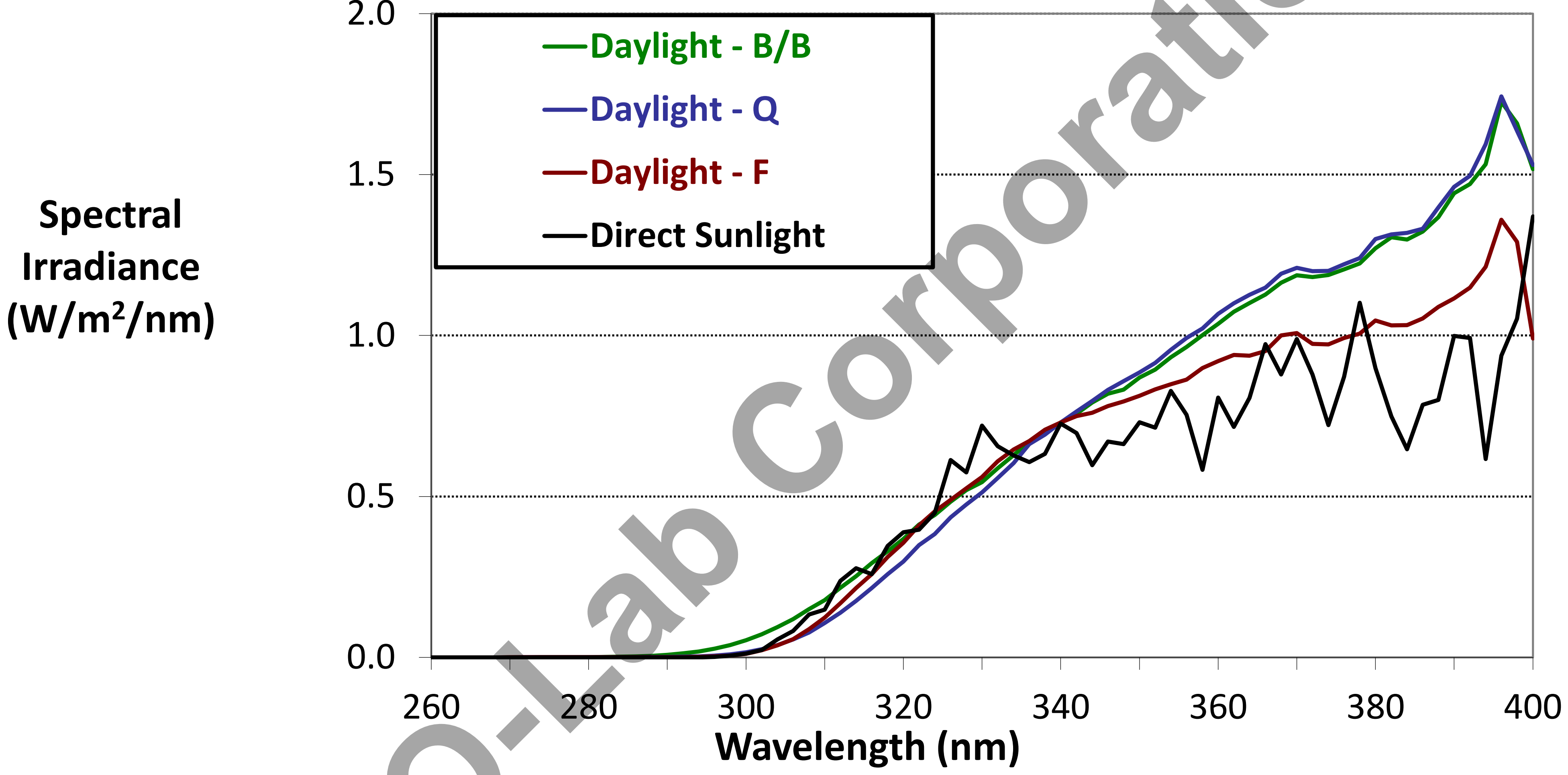
Xenon Arc with Daylight Filters

UV and Visible



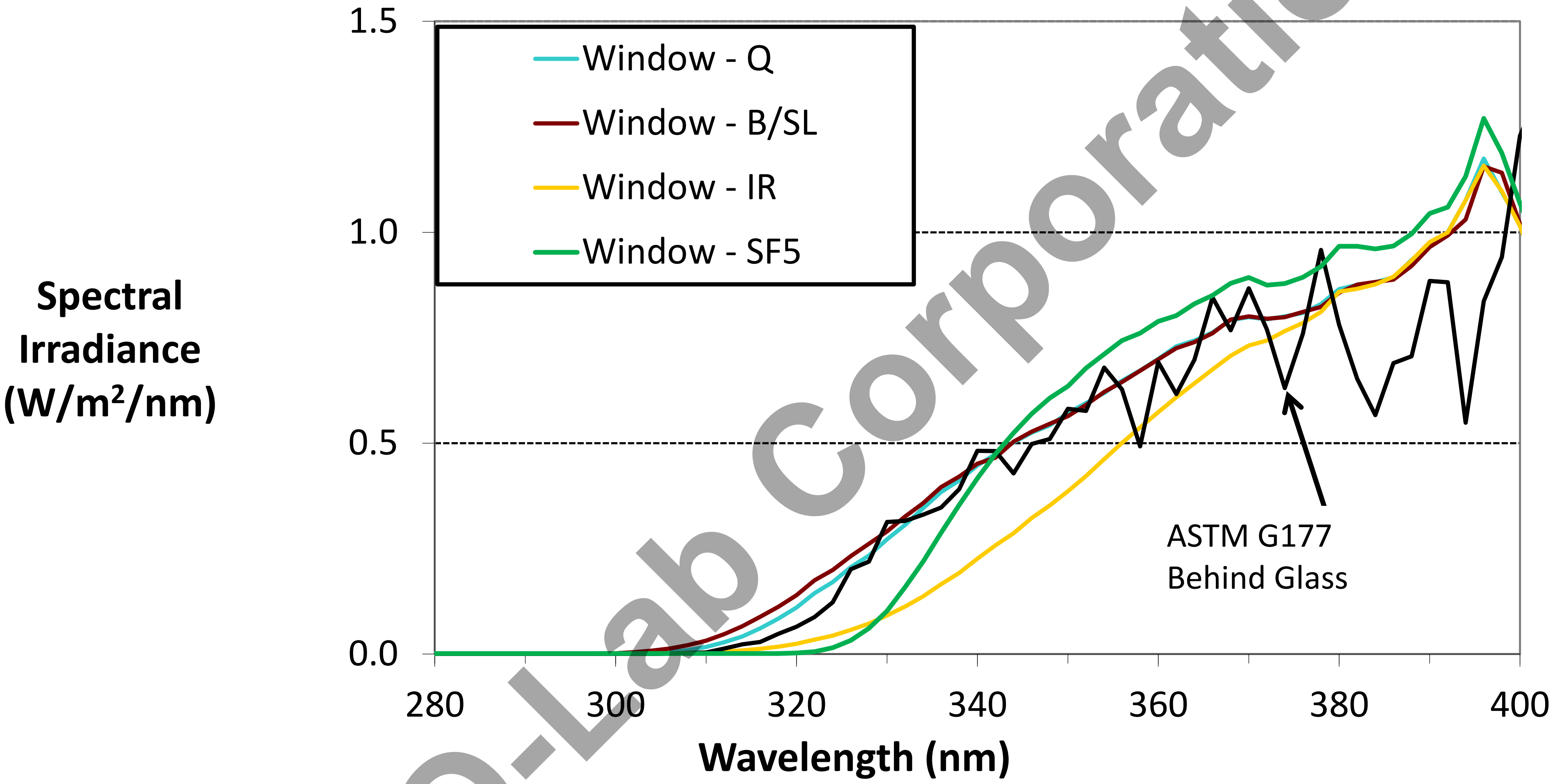
Xenon Arc with Daylight Filters

UV spectrum



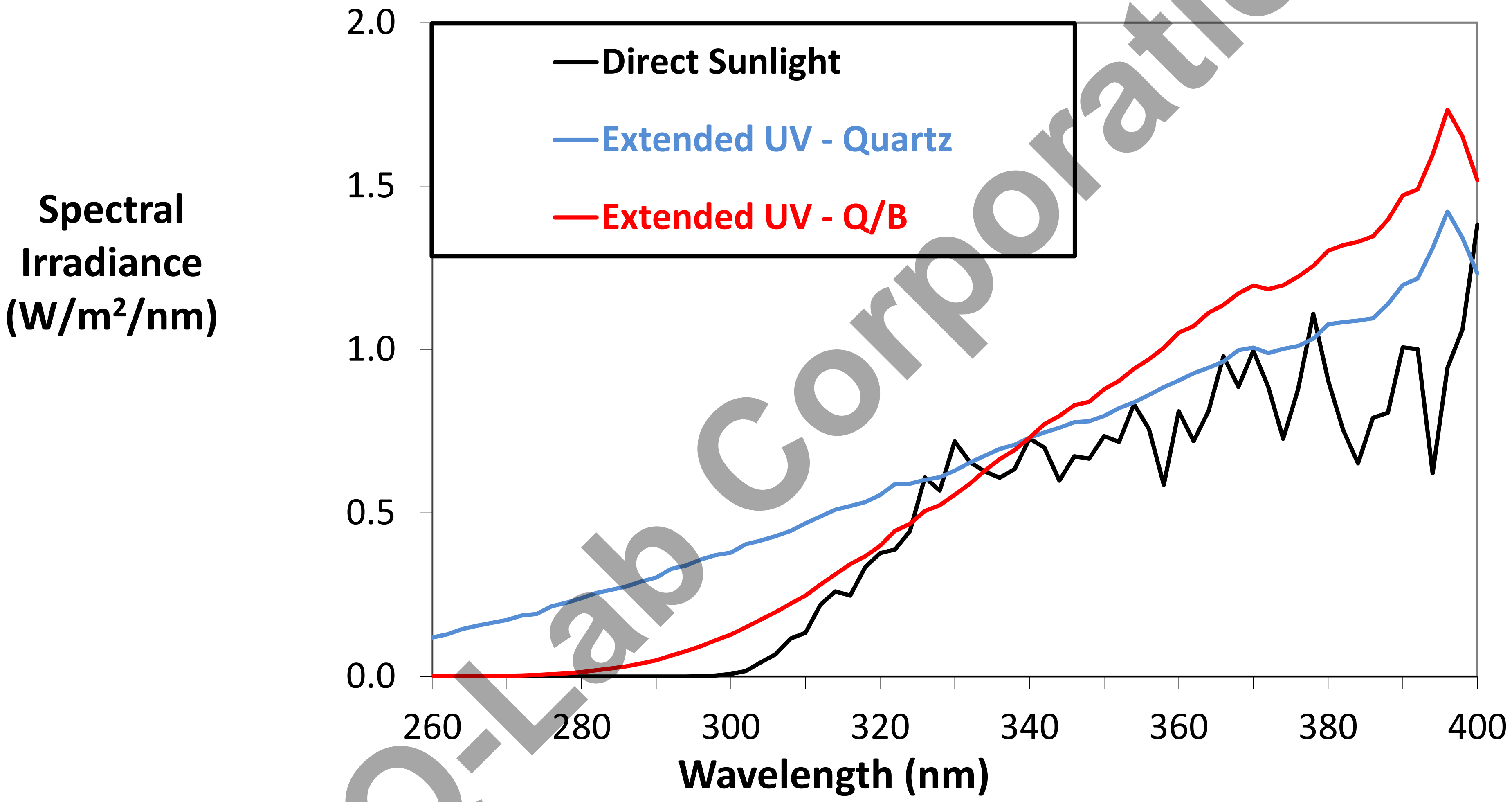
Xenon Arc with Window Filters

UV Spectrum



Xenon Arc with Extended UV Filters

UV Spectrum



Q-SUN SOLAR EYE^{TM} Irradiance Control

Feedback Loop Control

- Xenon-arc lamp
- Light sensor
- Control module

Wavelength at which irradiance is controlled is referred to as **Control Point**

Irradiance Control Point Options

Narrow Band

- 340 nm
- 420 nm

Wide Band

- Total UV TUV (300-400 nm)
- UV+VIS (300-800 nm)
  - Shorter wavelengths cause more photodegradation
  - Fails to account for xenon lamp aging

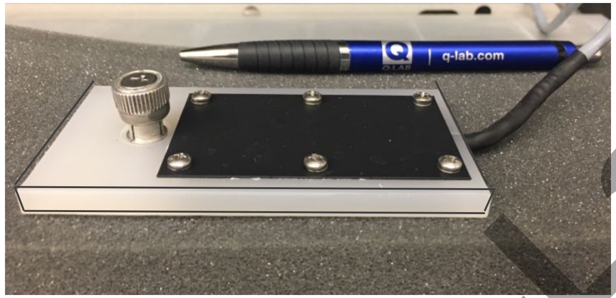
Why Is Choice of Control Point Important?

- Xenon Arc lamps age with use
- Spectral shift limits useful lamp life
- Controlling irradiance in **wavelength region of interest** maximizes repeatability and reproducibility

Black Panel Temperature Control

- Most common in test standards
- Approximates maximum specimen surface temperature
- Can be used in combination with chamber air temp sensor and control

Black Panel Temperature Sensors

Panel	Construction	ASTM Designation	ISO Designation
	Black painted stainless steel	Uninsulated Black Panel	Black Panel
	Black painted stainless steel mounted on 0.6 cm white PVDF	Insulated Black Panel	Black Standard

** White Panel versions of the above are available but far less commonly used*

To **maximize** acceleration,
use maximum service temperature

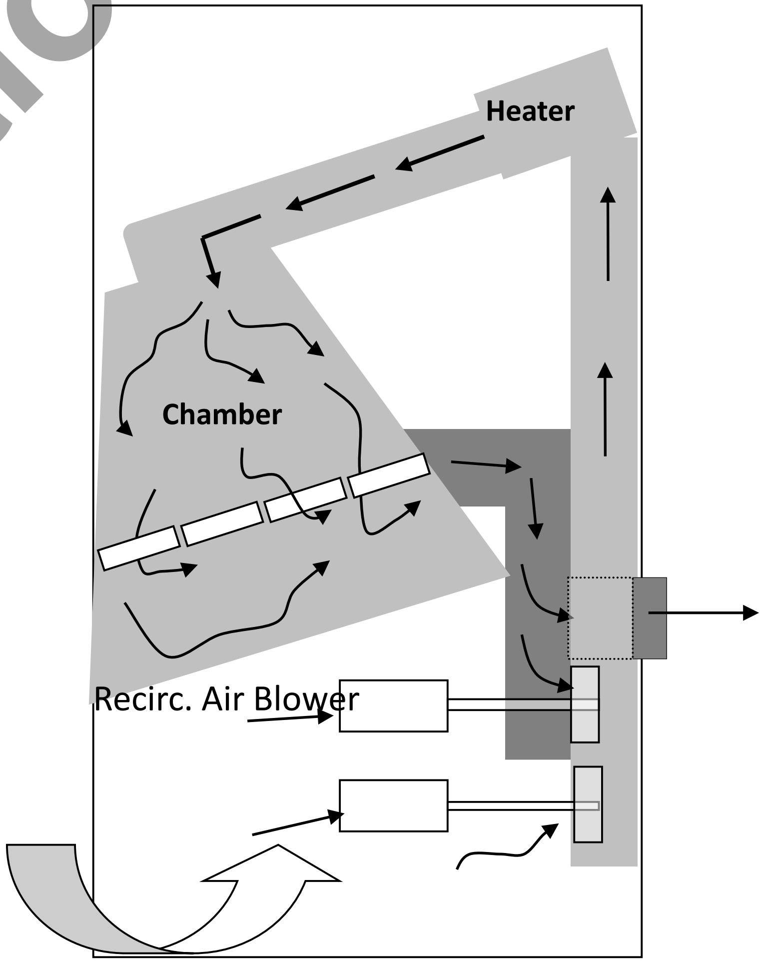
To **minimize** error, *DO NOT* exceed
maximum service temperature

Chamber Air Temperature Control

- Required by certain test methods
- Necessary for control of relative humidity (RH)
- Sensor must be shielded from light
- BP temp always hotter than chamber air temp from absorbing radiant heat

Relative Humidity Control

- Required by many test methods
  - Plastics, textiles, general use
  - Automotive (SAE)
- Many xenon testers can generate and control relative humidity
  - Boiler-type system
  - Nebulizer system
- For plastics, RH typically makes very little difference compared to spray and condensation



Water Spray

Front spray

- Primary method of water delivery
- Calibration technique for front spray recently developed (ASTM D7869)

Back spray

- Result of a failed experiment intended to generate condensation; persists in some standards

Dual spray

- For delivering a 2nd solution, e.g. acid rain, soap

Immersion (Ponding)

- Alternative to front spray used in some standards

Xenon Arc Summary

- Best simulation of full-spectrum sunlight
- Lamps experience aging (fulcrum effect)
- Temperature effects
- Water spray and RH control
- Additional cost, maintenance, and complexity compared to fluorescent UV testers

Q-SUN Xenon Arc Testers

Xe-1

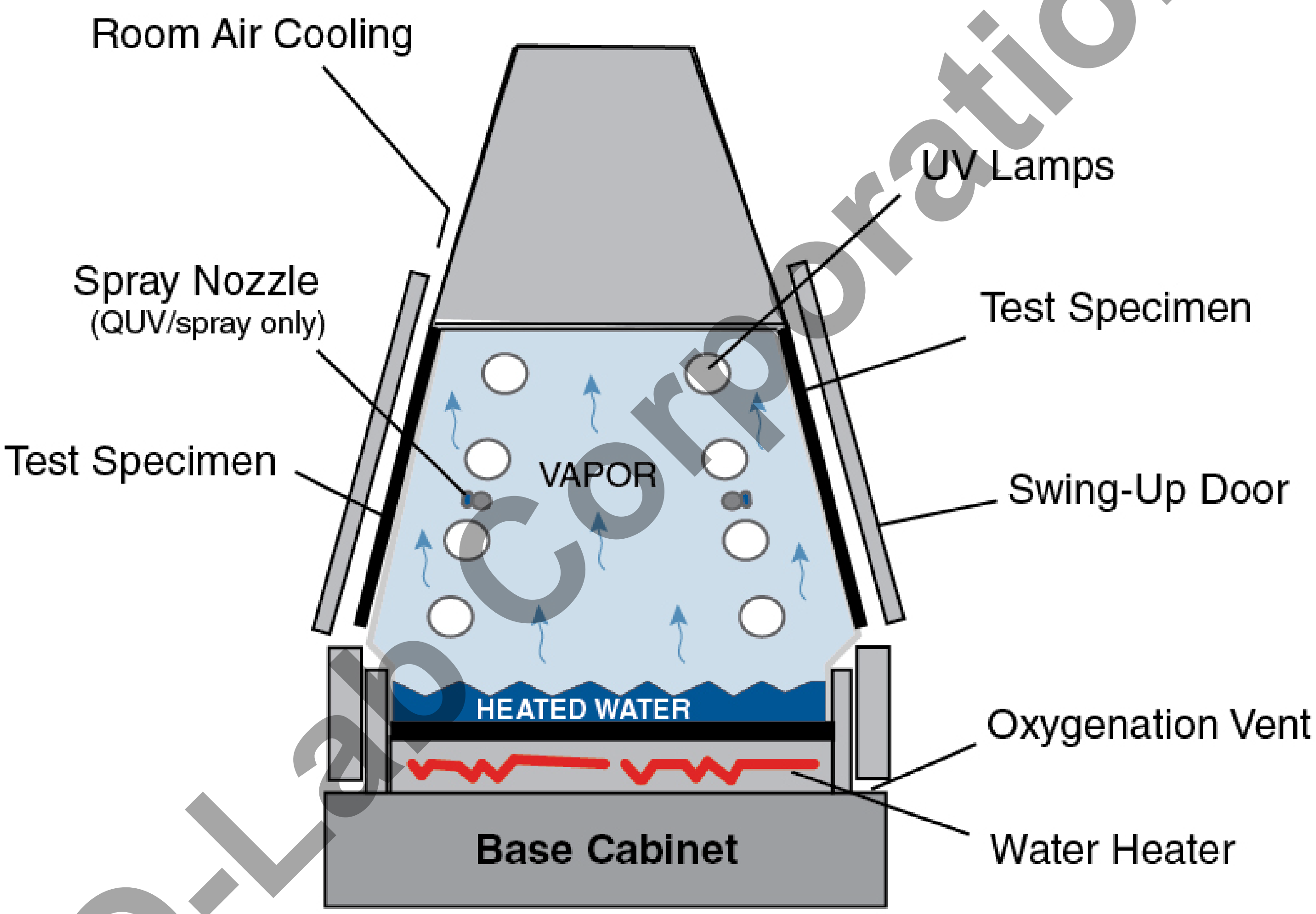
Xe-2

Xe-3

Fluorescent UV

Laboratory Weathering Testing

Fluorescent UV Schematic

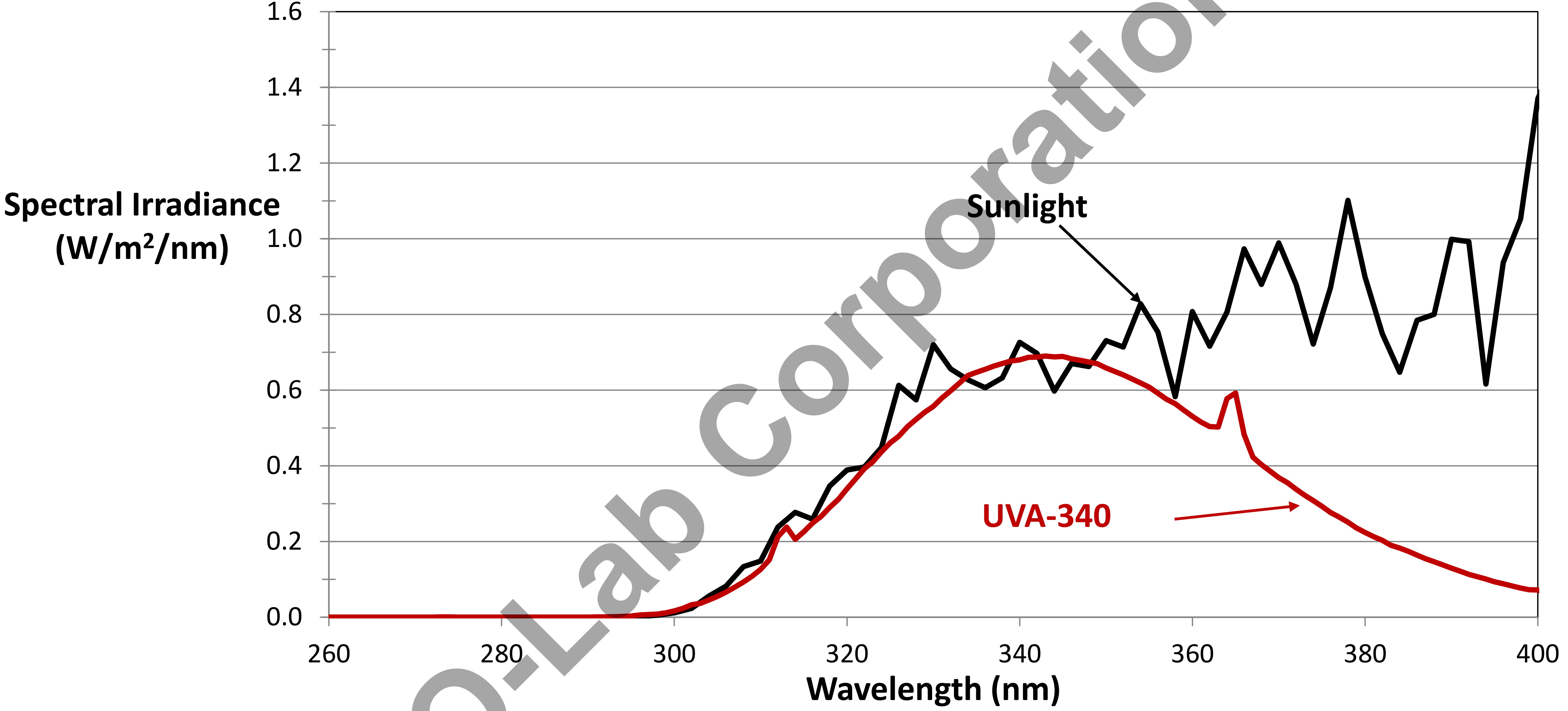


Fluorescent UV Lamps

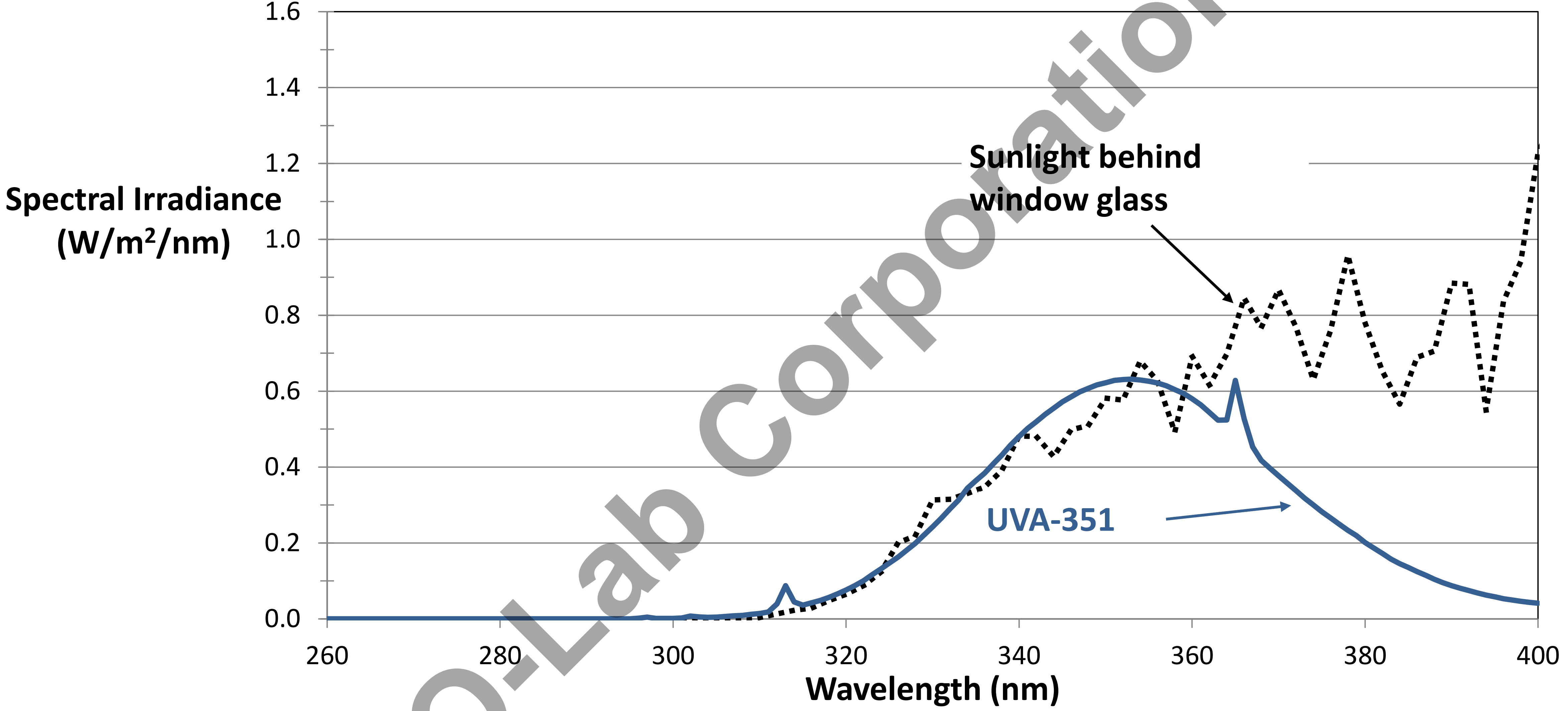
QUV Lamp Summary

- UVA-340 (Daylight UV)
- UVA-351 (Window UV)
- UVB-313EL/FS-40 (Extended UV)
- UVC-254
- Cool White (Indoor)

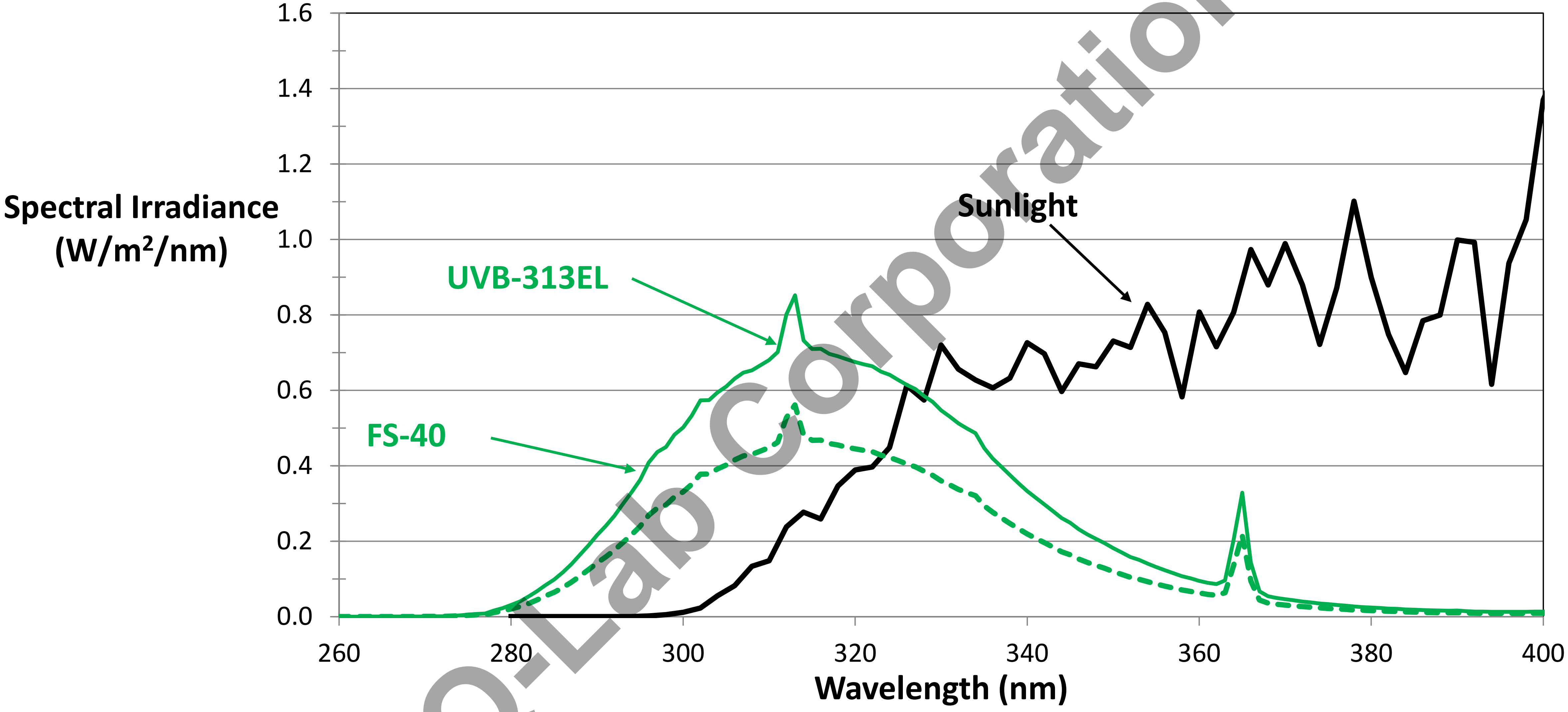
UVA-340 Lamps



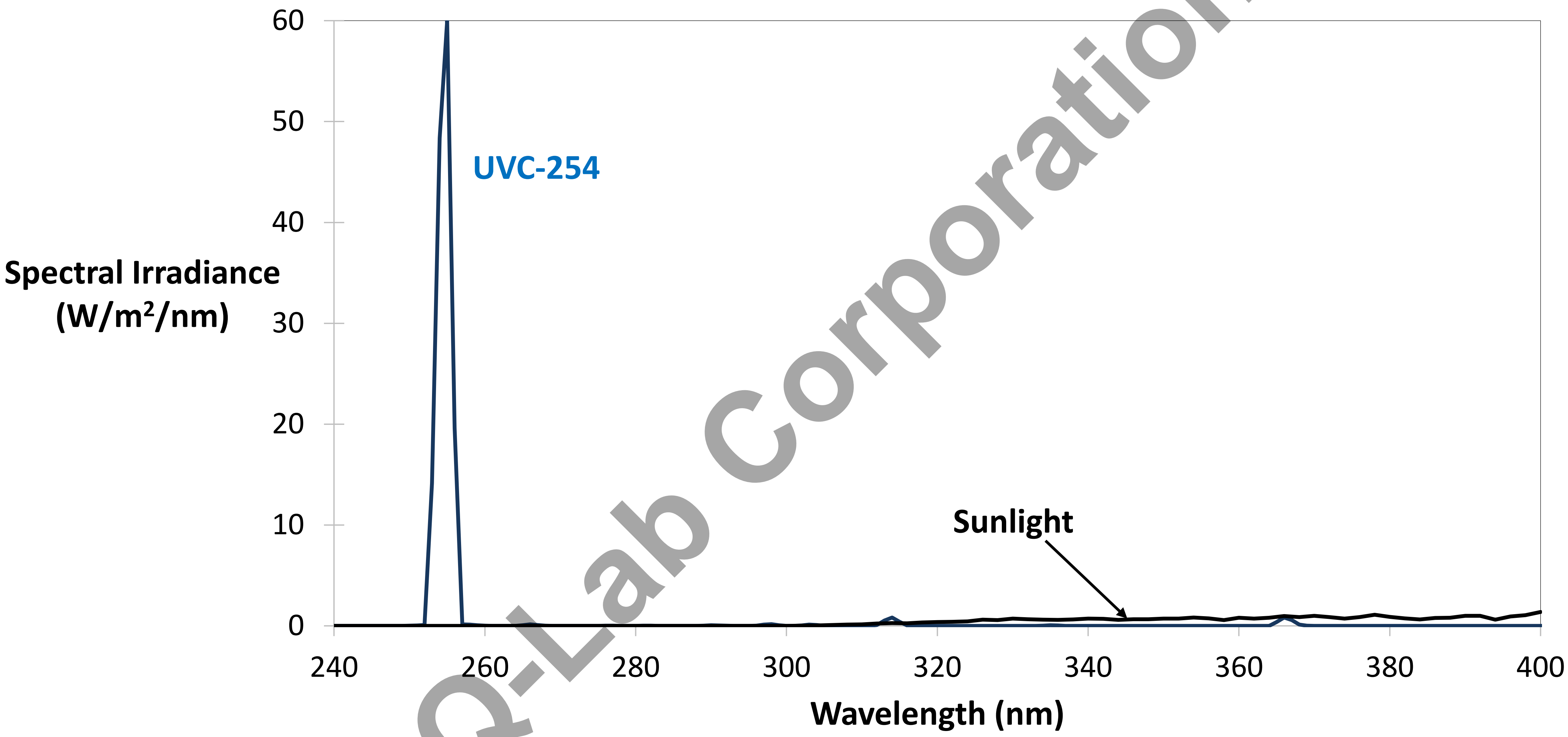
UVA-351 Lamps



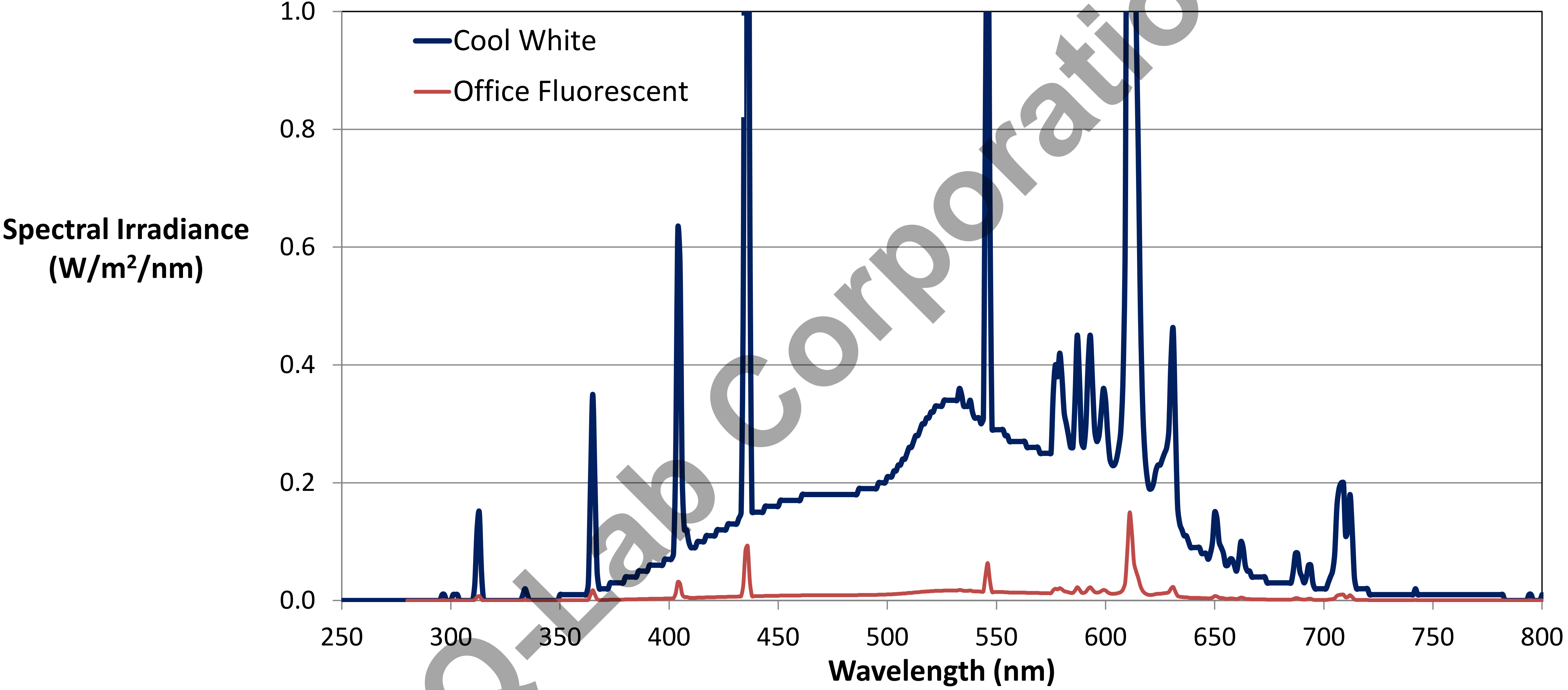
UVB Lamps


Spectral Irradiance (W/m²/nm)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
UVB-313EL
FS-40
Sunlight
260
280
300
320
340
360
380
400
Wavelength (nm)

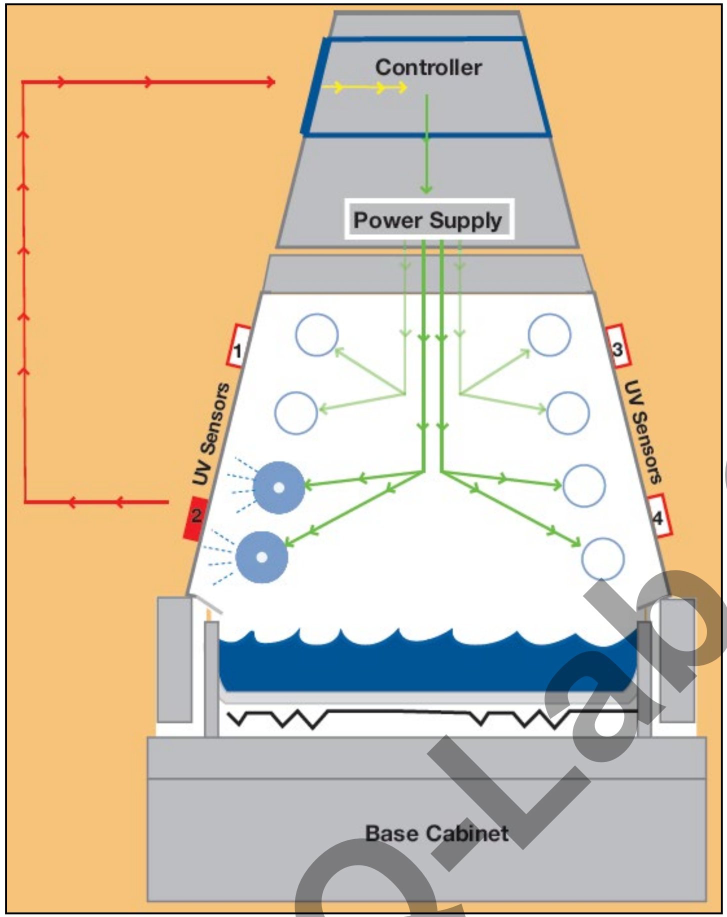
UVC Lamps


60
50
40
30
20
10
0
Spectral Irradiance (W/m²/nm)
UVC-254
Sunlight
240
260
280
300
320
340
360
380
400
Wavelength (nm)

Cool White Lamps



QUV SOLAR EYE™
Irradiance Control



Feedback Loop Control

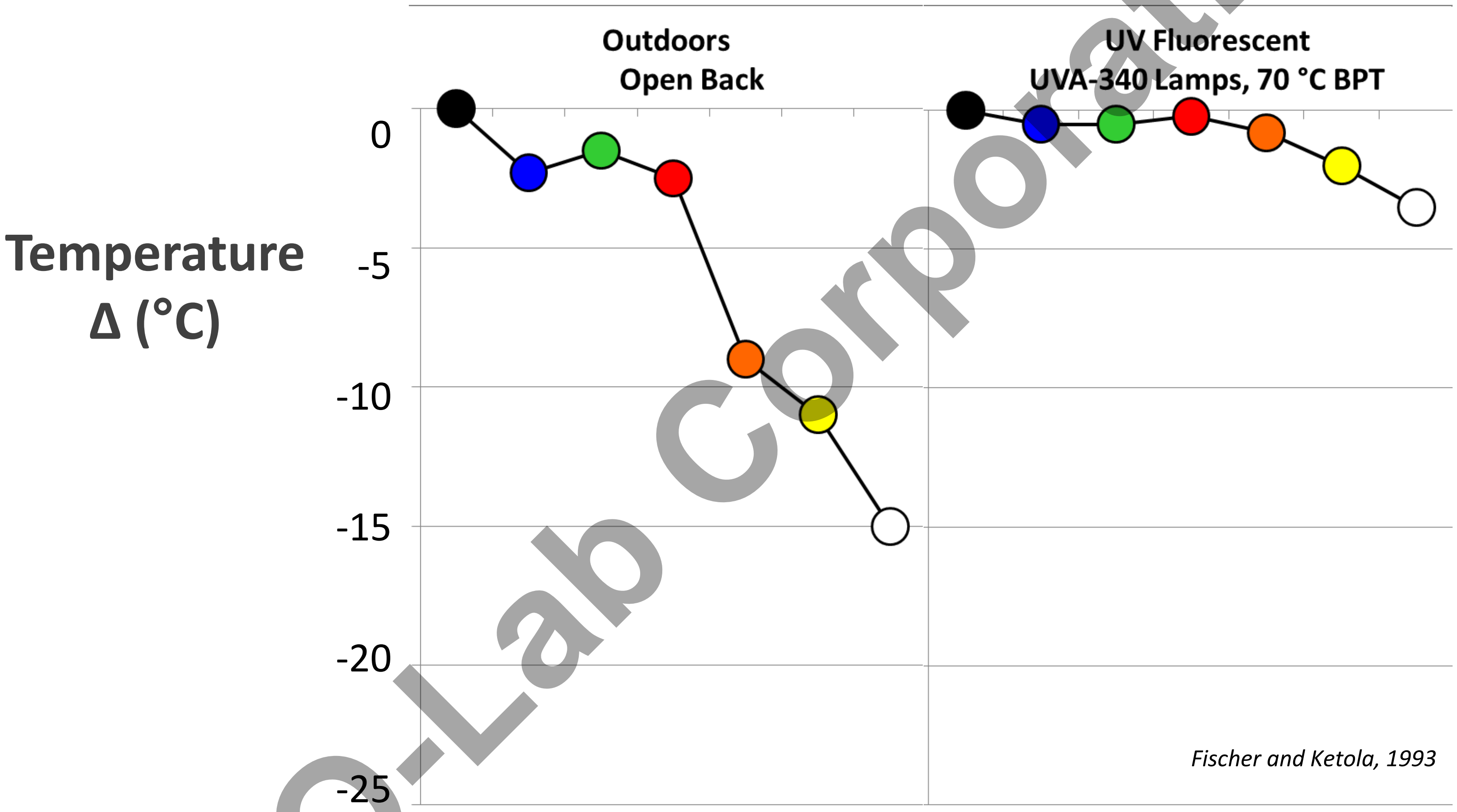
- Fluorescent UV lamp
- Light sensor
- Control module

Fluorescent Lamp Advantages

- Fast Results
- Simplified irradiance control
- Very stable spectrum – no aging
- Low maintenance
  - Simple calibration
- Low price and operating cost
- Simple and easy to maintain

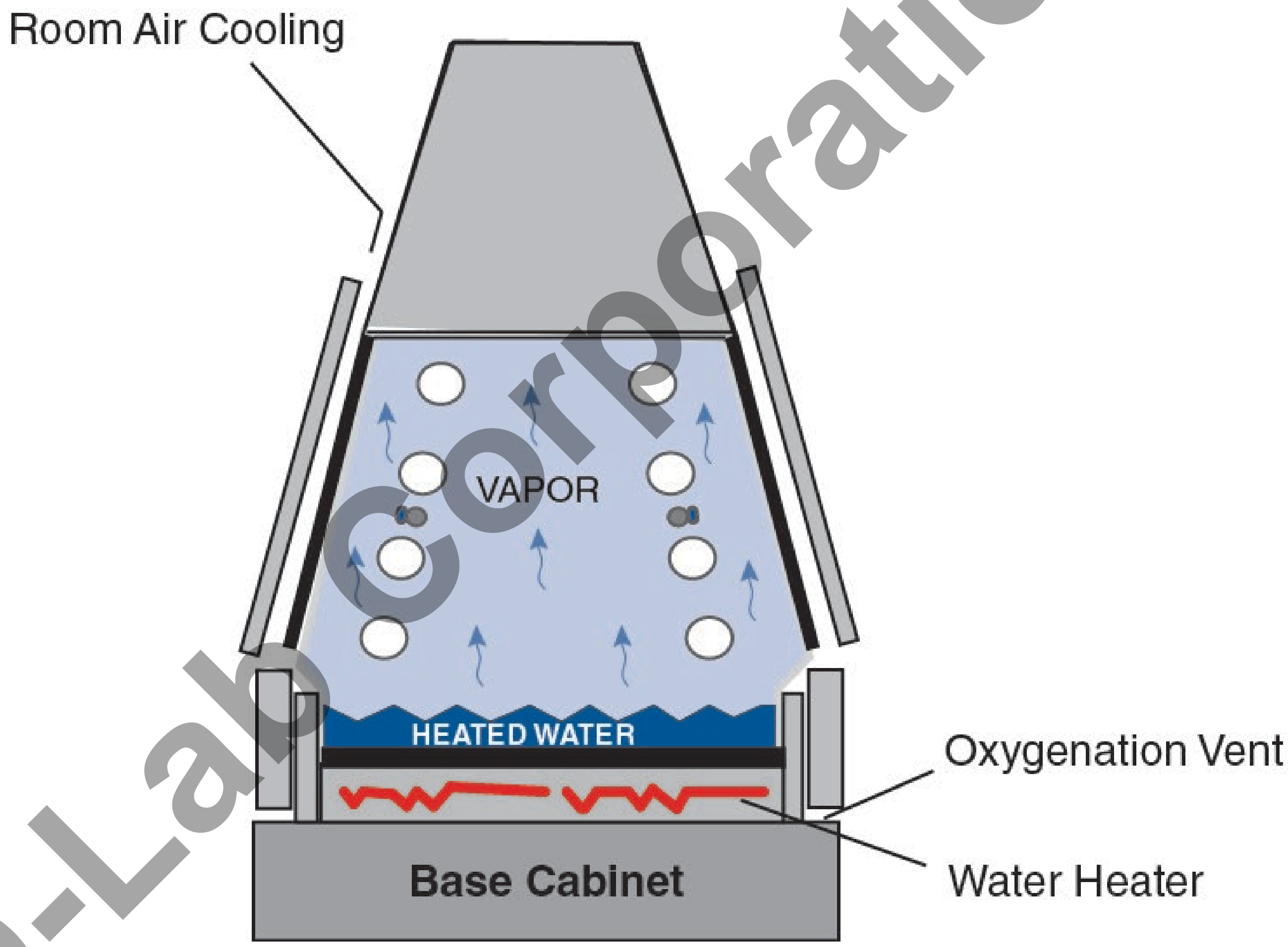
Temperature & Color

Temperature difference between colored panels and Black Panel



Fischer and Ketola, 1993

Condensation



Condensation Advantages

- Closest match to natural wetness
- Best way to accelerate water in an laboratory tester
- Elevated temperature
- High O_2 content
- Tester performs distilling – you cannot deposit debris on specimens! Water is guaranteed to be clean.

Creating condensation in the QUV is easy and does not require expensive, pure water

Water Spray

- Ensures that parts get fully saturated
- Creates erosion & thermal shock

Creating spray in the QUV is difficult and relatively expensive

Fluorescent UV Summary

- UVA-340 best simulation of short-wave UV
- UVB-313 fastest & most severe
- Stable spectrum – no aging
- No visible light
- Condensation realistic & rigorous
- Water spray available but not RH control

QUV Accelerated Weathering Tester

Model QUV/se

Laboratory Weathering Testing

- Basics of Weathering
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  - –Fluorescent UV
- **Elements of an Effective Testing Program**

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Predictive	Service life Acceleration factor	• Open-ended • Long	Natural exposure (Service environment)

Fluorescent UV and Xenon Arc

Complementary Technologies

Fluorescent UV	Xenon Arc
• UVA-340 best simulation of shortwave UV	• Full spectrum (UV-Vis-IR)
• UVB-313 might be too severe • No visible light	• Best simulation of long wave UV & visible light
• Stable spectrum	• Spectrum changes
• No RH control	• RH control
• Condensation or water spray	• Water spray
• Inexpensive, simple to use	• More complex system

Putting It All Together

- Identify the kind of accelerated test
  - Outdoor data is imperative for both correlative and predictive testing
- Identify service environment
  - Indoor or Outdoor
  - Wet or Dry
  - Hot or Cool

Putting It All Together

- Use Best Practices
  - Run until a defined failure mode
  - Use multiple replicates
  - Perform evaluations and reposition frequently

- Pick an appropriate Test Architecture
  - What does the standard say?
  - Is full spectrum important?
  - How important is water uptake?

Questions?

info@q-lab.com