Ductile-to-Brittle
Transitions in Plastics

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February 8, 2023

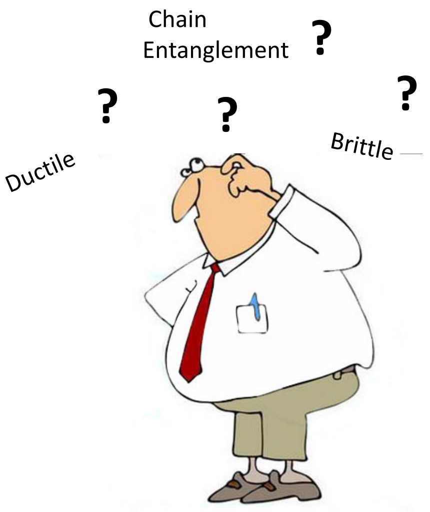
Goal

To address questions that arise regarding plastic component failure:

- Why do I experience sudden unexpected failure in my plastic components?
- Why do the properties of my plastic parts change?
- Why do I get brittle failures in my ductile material?

Agenda

- Cracking in Plastics
- Viscoelasticity
- Temperature
- Strain Rate
- Time Under Load
- Chemical Contact – ESC
- Dynamic Stress
- Molecular Weight
- Molecular Degradation
- Molecular Fusion
- Stress Concentration

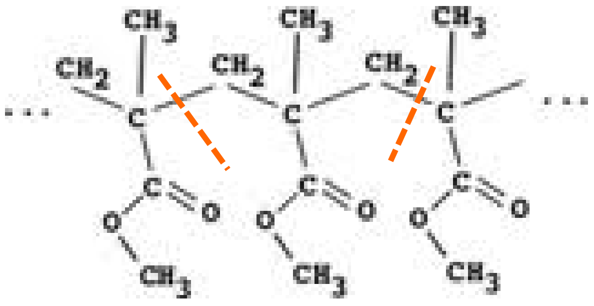


CRACKING IN PLASTICS

Plastics Cracking

Characteristics of Plastics Cracking:

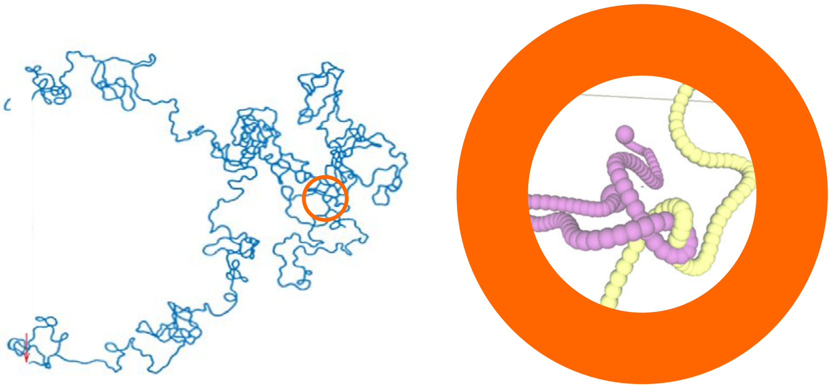
- Covalent polymer backbone bonds are not broken by mechanical forces



Plastics Cracking

Characteristics of Plastics Cracking:

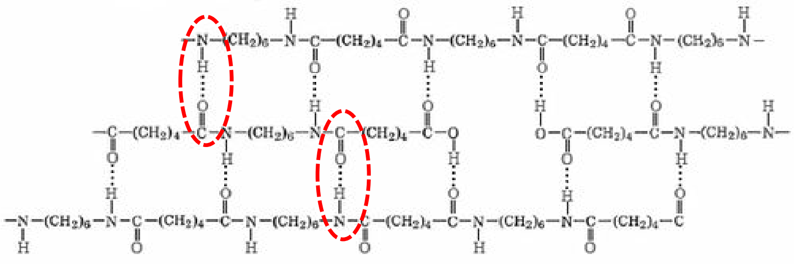
- Disentanglement mechanism in which polymer chains slide past each other



Plastics Cracking

Characteristics of Plastics Cracking:

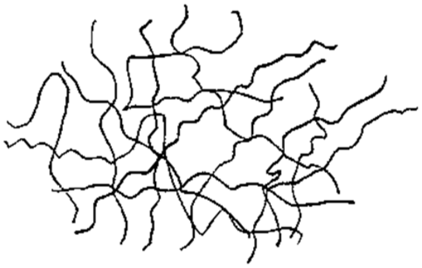
- Applied stresses – both internal and external - overcome inter-molecular forces such as, Van der Waals forces, London dispersion forces, hydrogen bonding, and dipole interactions



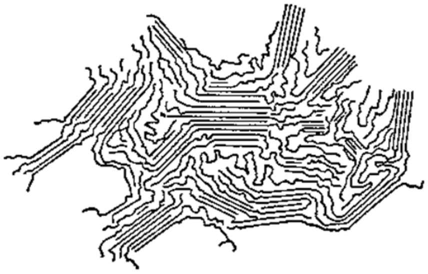
Plastics Cracking

Characteristics of Plastics Cracking:

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

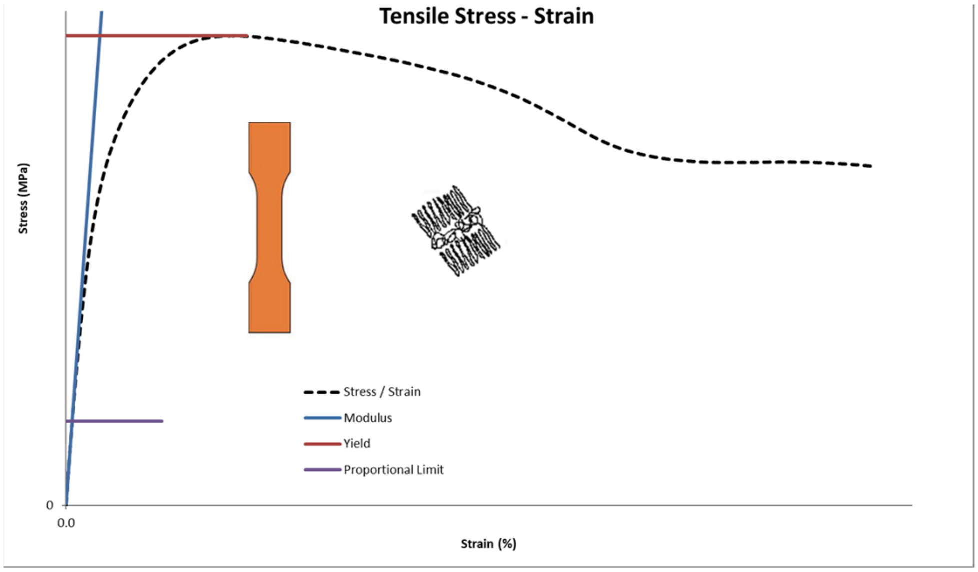


Amorphous

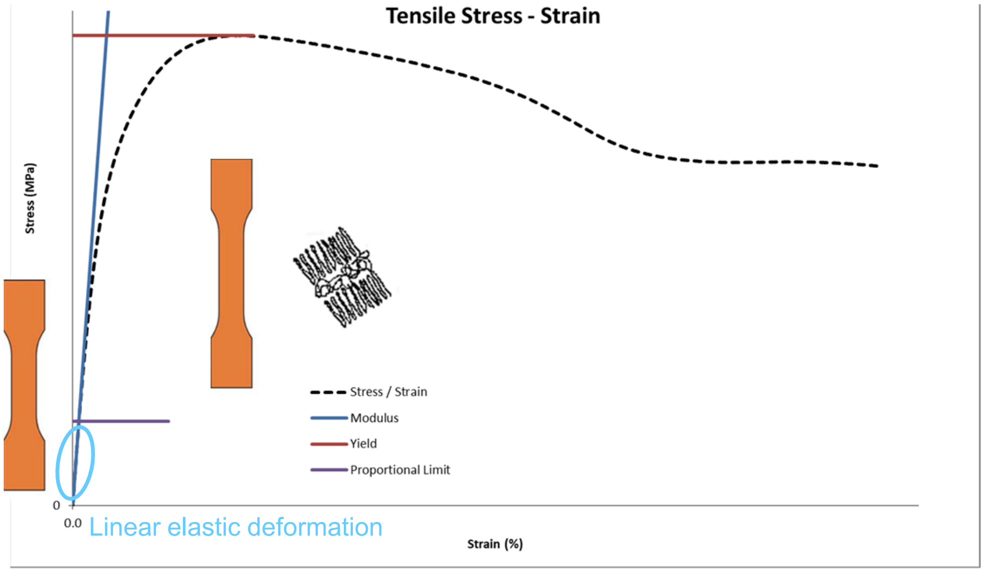


Semi-crystalline

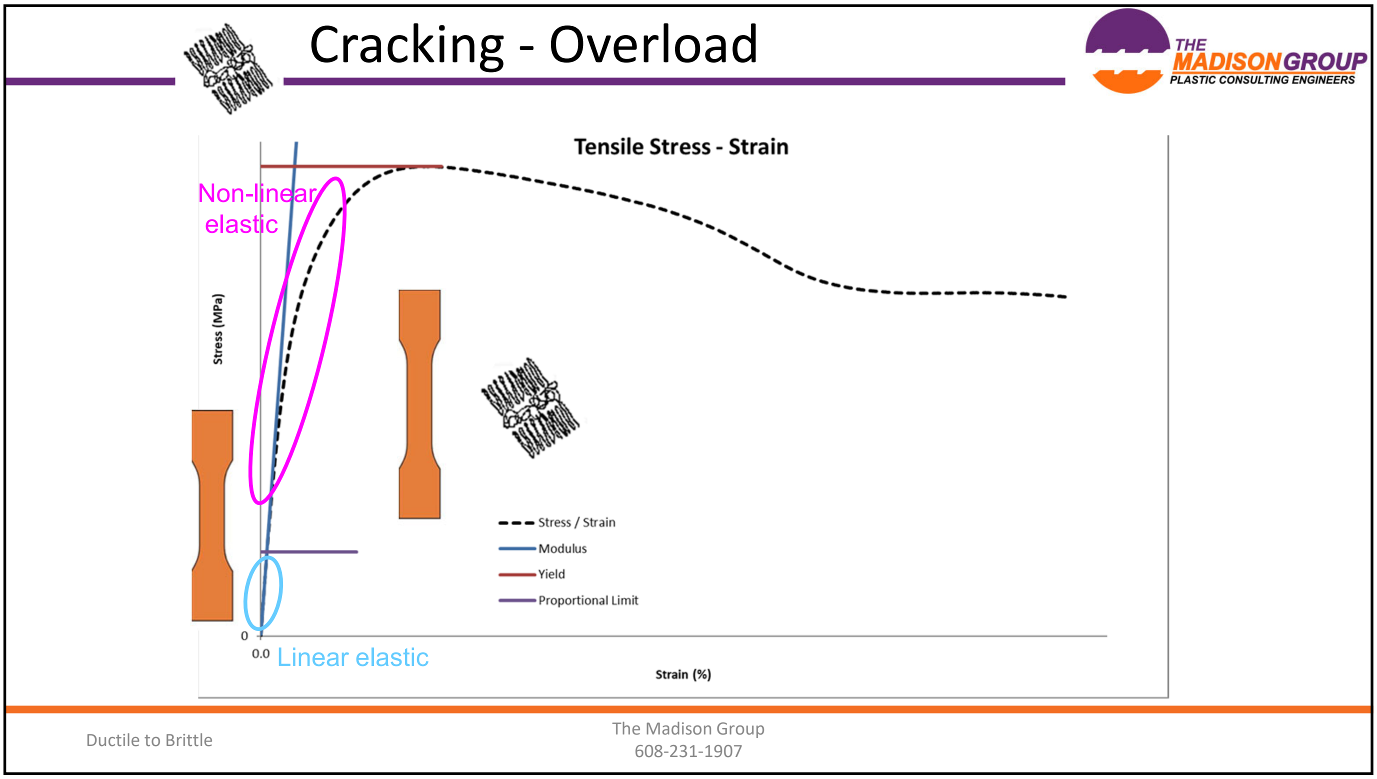
Cracking - Overload



Cracking - Overload



Linear elastic deformation



Cracking - Overload

Ductile to Brittle

The Madison Group
608-231-1907

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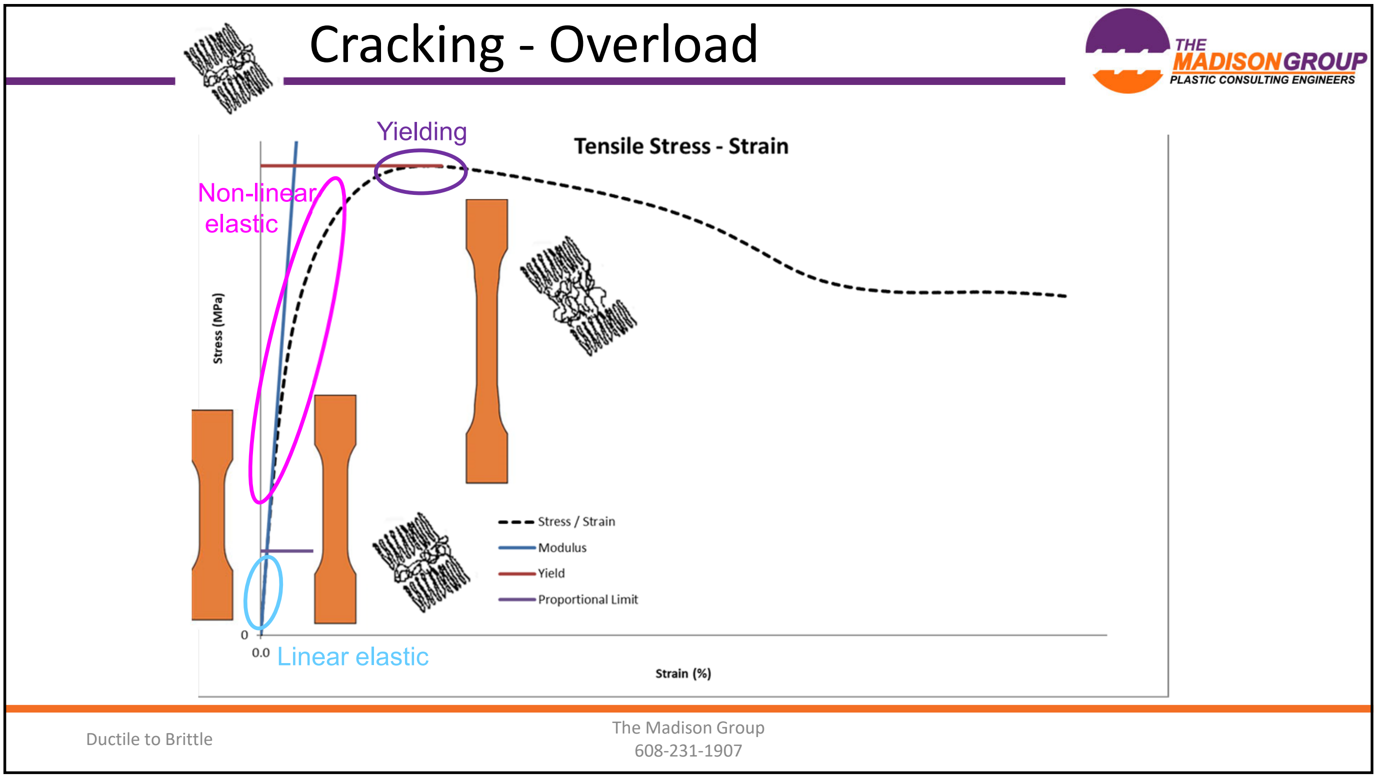

Cracking - Overload

Ductile to Brittle

The Madison Group
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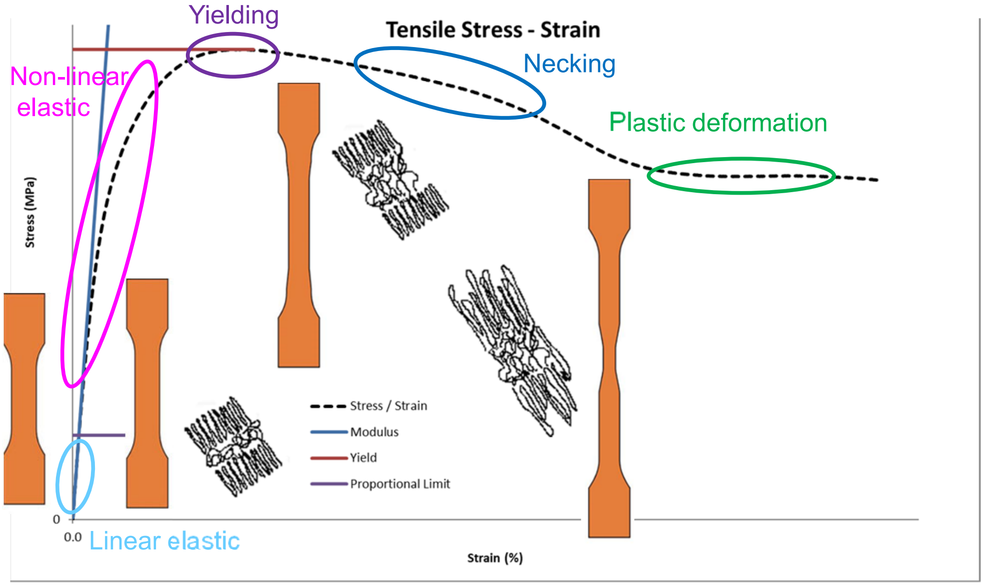
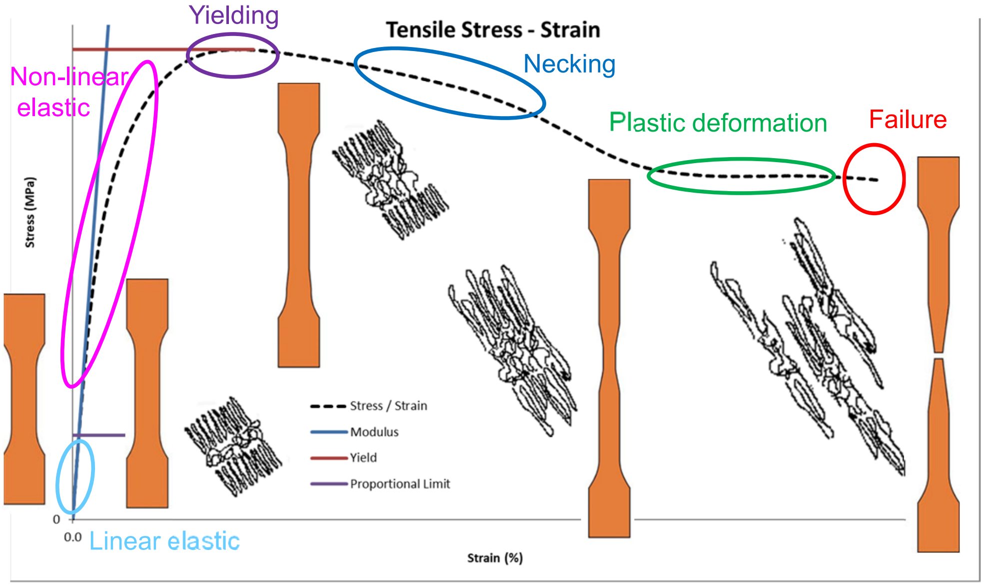
Cracking - Overload



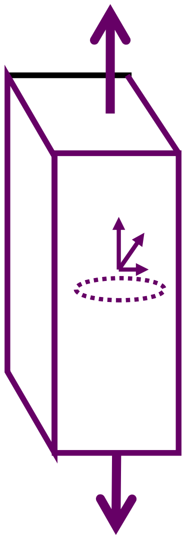
Cracking - Overload



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

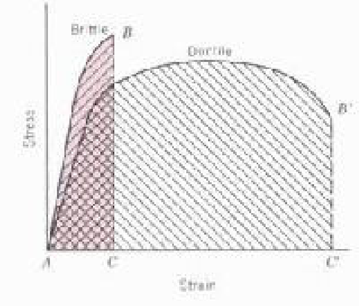


Plastics Cracking

Brittle vs. Ductile Fracture

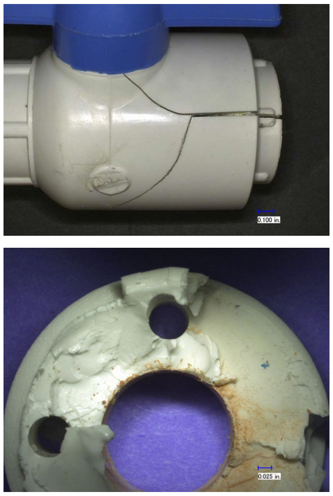
- Ductile fracture - *extensive plastic deformation* and energy absorption (“toughness”) before fracture

- Brittle fracture - *little plastic deformation* and low energy absorption before fracture

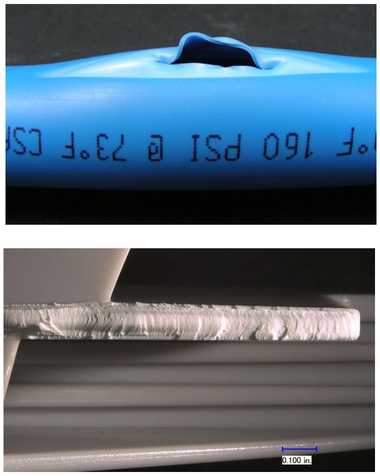


Plastics Cracking

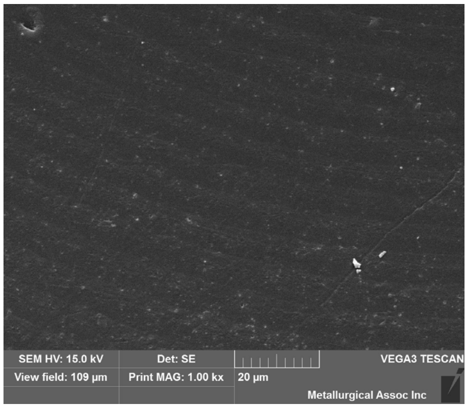
No Macro-Ductility



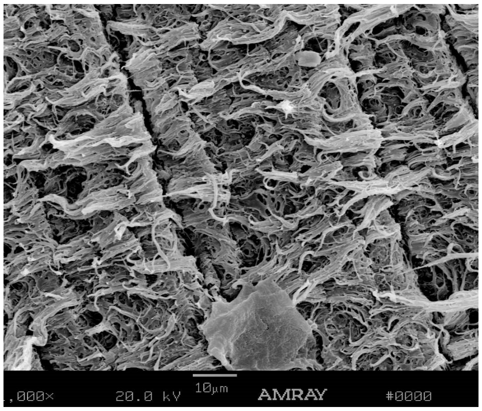
Macro-Ductility



Plastics Cracking



No Micro-Ductility



Micro-Ductility

Plastics Cracking

Most Failures Represent Brittle Behavior of a Normally Ductile Plastic

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

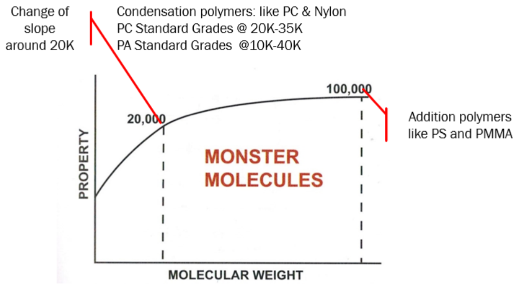
- Reduced Temperature
- Elevated Strain Rate
- Extended Time Under Load
- Dynamic Stress Loading
- Chemical Exposure
- Loss of Plasticizer
- Molecular Degradation

VISCOELASTICITY

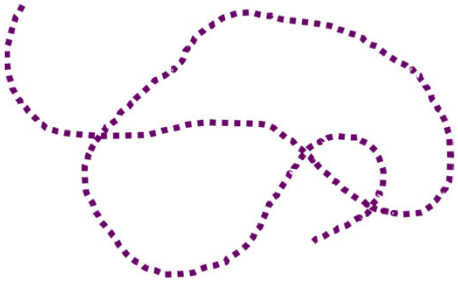
Viscoelasticity

Because of their molecular structure, polymeric materials have different properties compared to other materials, like metals.

The polymer molecules consist of very long chains – high molecular weight.



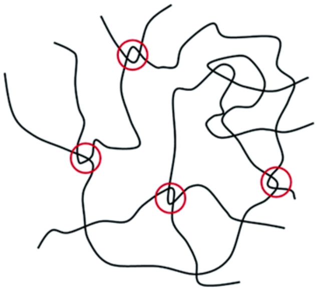
Ref: Ezrin, Plastics Failure Guide



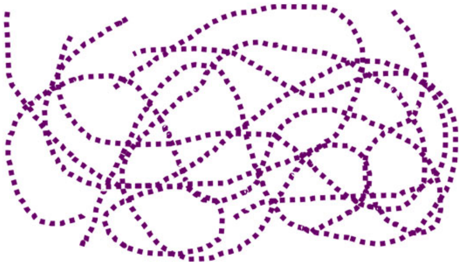
Viscoelasticity

Because of their molecular structure, polymeric materials have different properties compared to other materials, like metals.

The individual polymer chains are entangled in each other.



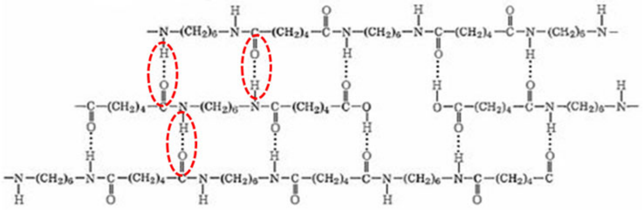
Topological entanglement

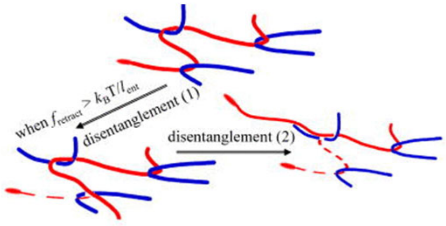


Viscoelasticity

Because of their molecular structure, polymeric materials have different properties compared to other materials, like metals.

The polymer chains are mobile and can slide past each other because they do not share chemical bonds with the other chains around them.





Viscoelasticity

- Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation.
- Viscous materials, like honey, resist shear flow and strain linearly with time when a stress is applied.
- Elastic materials, like a ~~rubber band~~ **steel rod**, strain when stressed and quickly return to their original state once the stress is removed.
- Viscoelastic materials have elements of both of these properties and, as such, exhibit time-dependent strain.

TEMPERATURE

Temperature

Temperature

- Lower temperature → lower ductility
- Kinetic energy
- Molecular response shifts to disentanglement/slippage away from yielding

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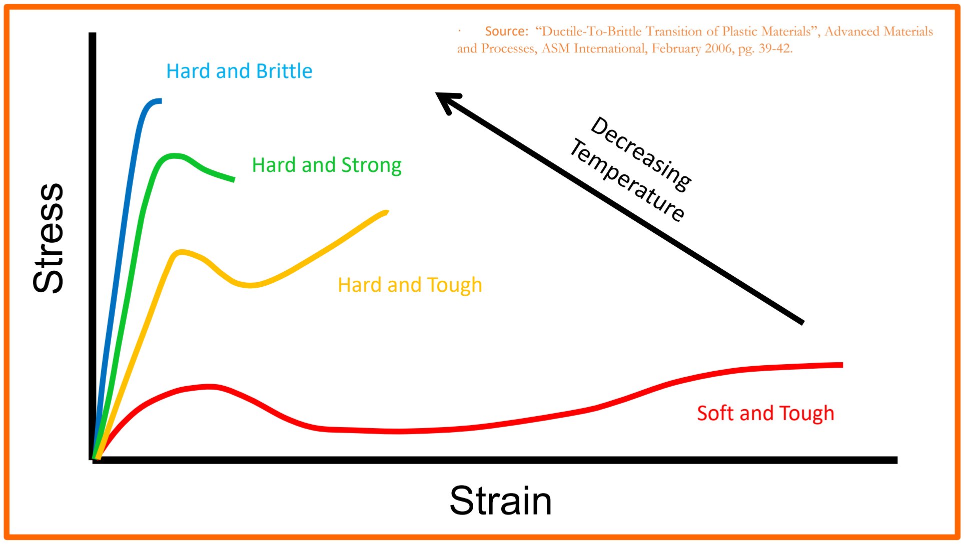
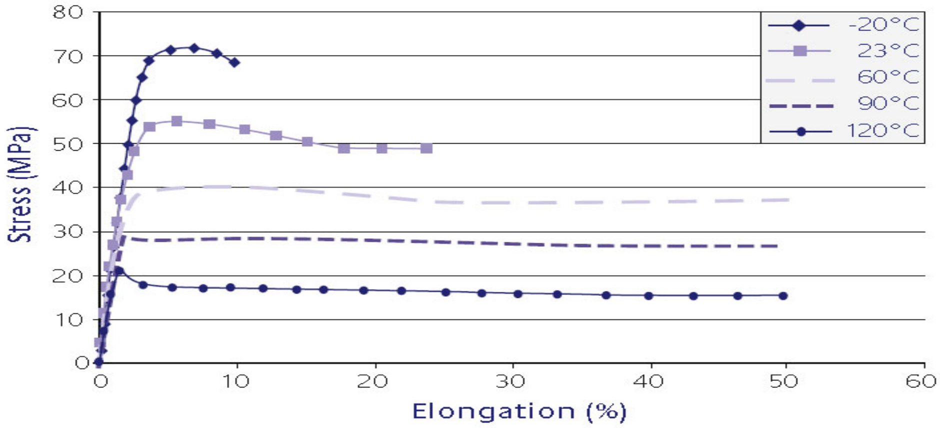
Temperature



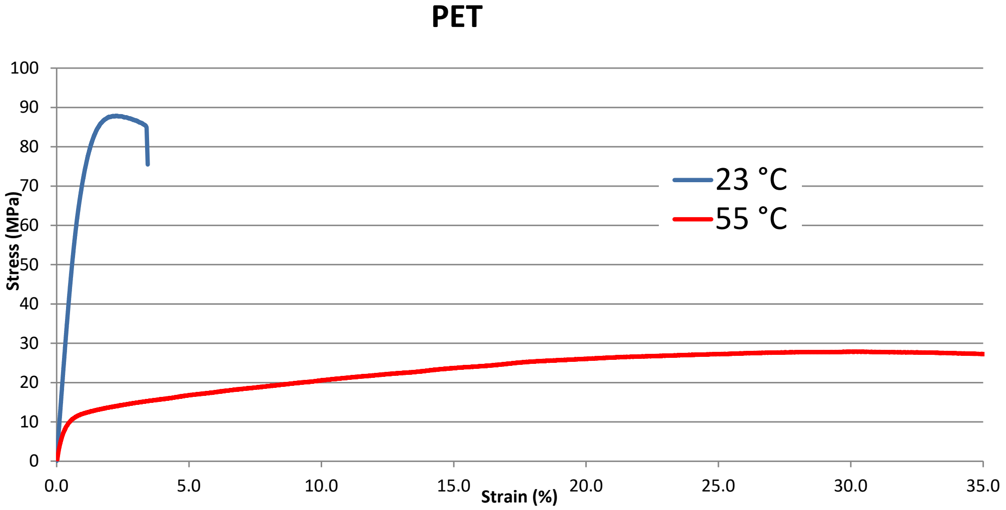
· Source: "Ductile-To-Brittle Transition of Plastic Materials", Advanced Materials and Processes, ASM International, February 2006, pg. 39-42.

Temperature

Noryl 731



Temperature

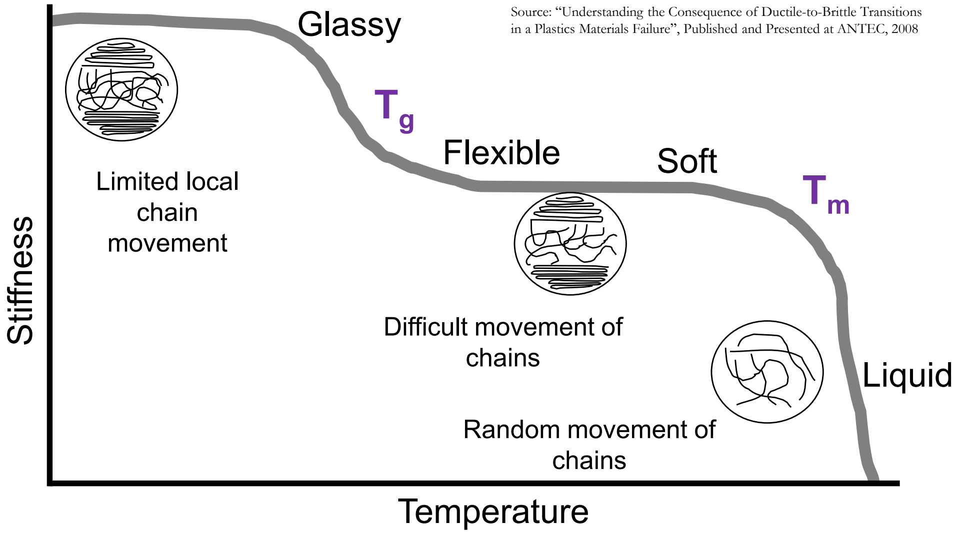


Temperature

Notched Izod Impact Strength

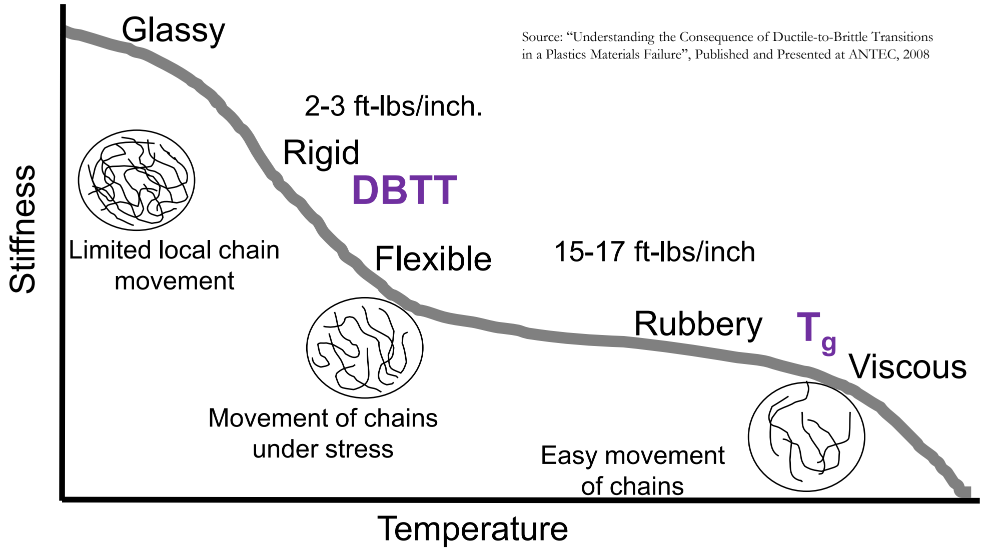
Temperature	Polycarbonate	ABS
73 °F	33 ft-lbs/in.^{2}	9 ft-lbs/in.^{2}
-22 °F	6 ft-lbs/in.^{2}	3 ft-lbs/in.^{2}

Temperature – Semi-crystalline



Source: "Understanding the Consequence of Ductile-to-Brittle Transitions in a Plastics Materials Failure", Published and Presented at ANTEC, 2008

Temperature – Amorphous

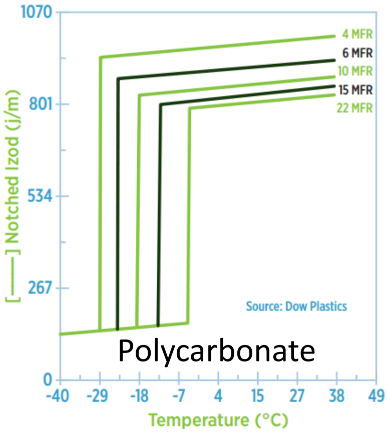


Source: "Understanding the Consequence of Ductile-to-Brittle Transitions in a Plastics Materials Failure", Published and Presented at ANTEC, 2008

Ductile-to-Brittle Transition

Measuring DBTT

ISO 6603-2 (multi-axial instrumented impact) across a temperature range.



Source: Dow Plastics

STRAIN RATE

Strain Rate

Characteristics of high strain rate cracking:

- Elevated strain rate → lower ductility
- Polymer chains slide past each other through disentanglement mechanism.
- At increasingly elevated strain rates, the polymer molecules making up the formed plastic component are precluded from having sufficient time to undergo plastic deformation and yielding.

Reduced impact properties

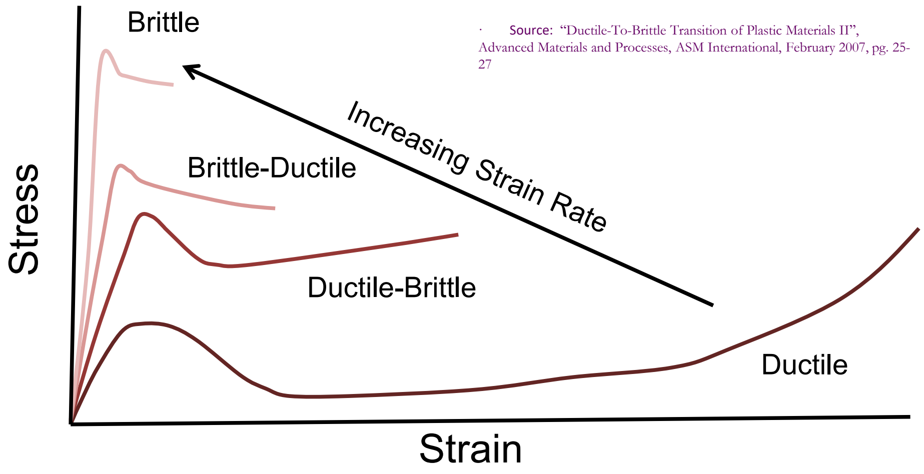
Reduced fracture toughness

Strain Rate

High Strain Rate Applications:

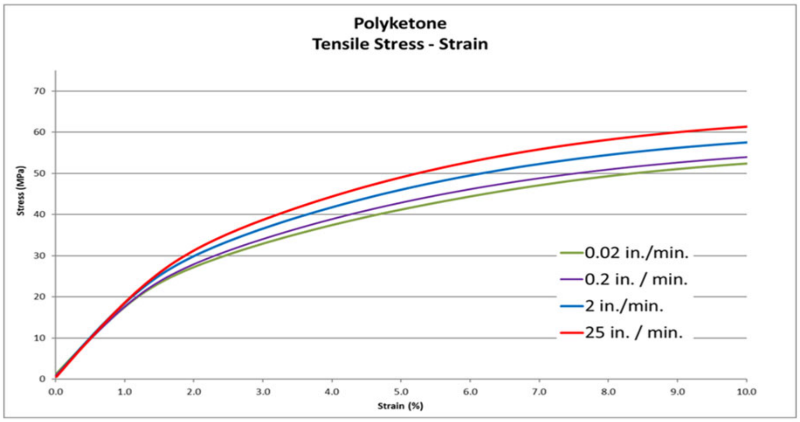
- Impact
- Snap-fit Installation
- Water Hammer / Rapid Pressurization

Strain Rate



· Source: "Ductile-To-Brittle Transition of Plastic Materials II", Advanced Materials and Processes, ASM International, February 2007, pg. 25-27

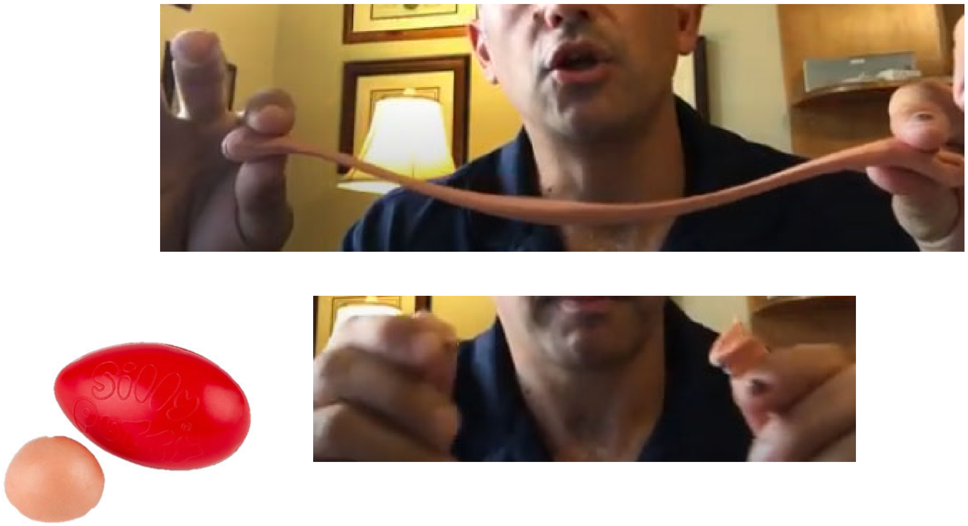
Strain Rate



Test Speed	Modulus (MPa)	Tensile Strength at Yield (MPa)	Elongation at Yield (%)	Elongation at Break (%)
0.02 in./min	1741	57.8	27.5	407
0.2 in./min.	1883	58.2	21.3	384
2 in./min.	2001	60.8	18.6	317
25 in./min.	2108	64.1	16.4	95

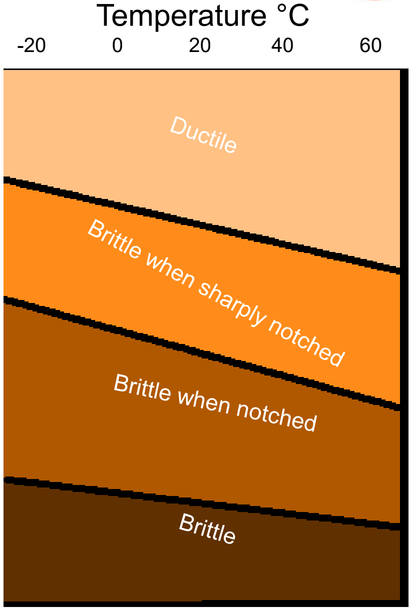
Strain Rate

Strain Rate

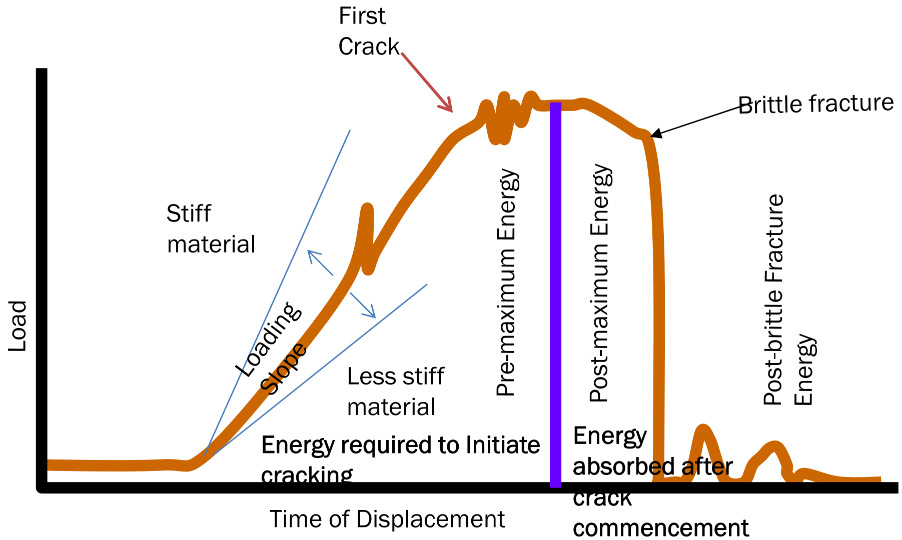


Strain Rate

Low density polyethylene
Nylon – wet
Polycarbonate
Acrylonitrile:butadiene:styrene resin
Polypropylene copolymers
High density polyethylene
Nylon – dry
Poly(vinyl chloride)
Polyacetal
Poly(ethylene terephthalate)
Polypropylene homopolymer
Poly(methyl methacrylate)
Polystyrene



Strain Rate



TIME UNDER LOAD

Time Under Load

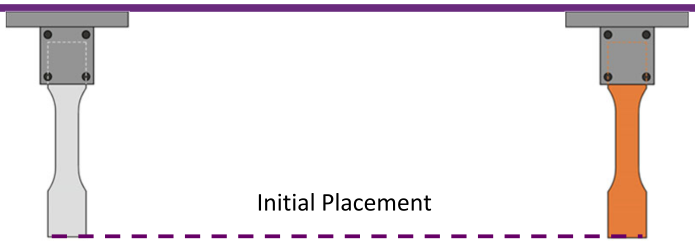
Creep is…..

the tendency of a solid material to deform permanently under the influence of constant stress (tensile, compressive, shear, or flexural). It occurs as a function of time through extended exposure to levels of stress that are below the yield strength of the material.

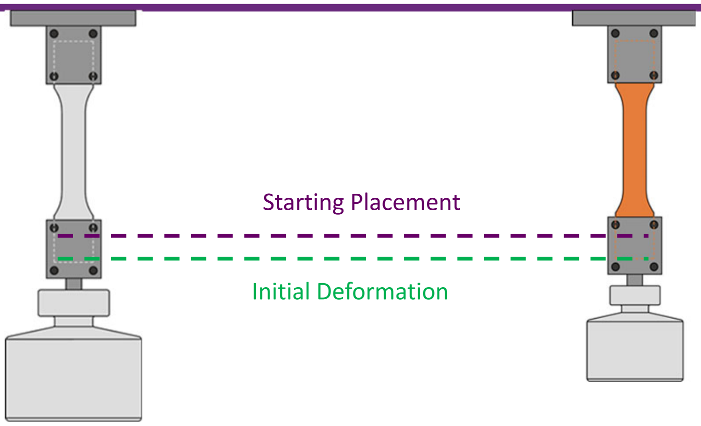
Time Under Load

- Low to moderate forces exerted over an extended time → lower ductility. Can result in brittle fracture in normally ductile plastics
- Inherent viscoelastic nature of polymers leads to time dependency
- Prolonged static stresses lead to a decay in apparent modulus through localized molecular reorganization of polymer chains
- At stresses below the yield point molecular reorganization includes disentanglement as there is no opportunity for yielding

Time Under Load

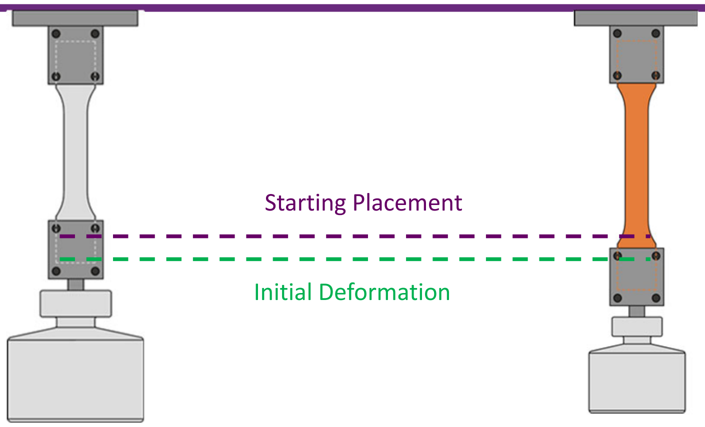


Time Under Load



Day 1

Time Under Load

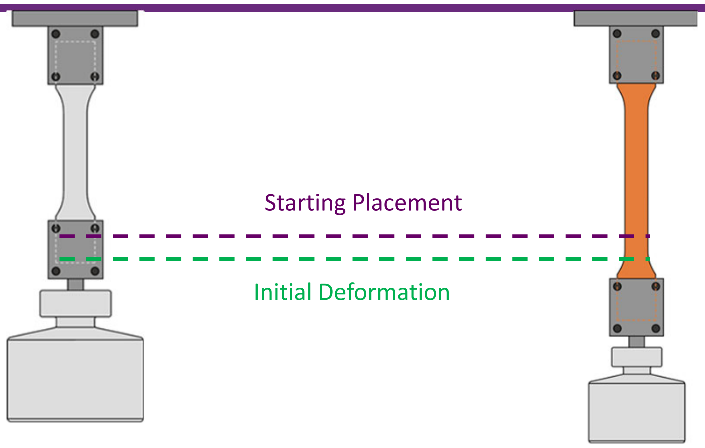


Starting Placement

Initial Deformation

Day 10

Time Under Load

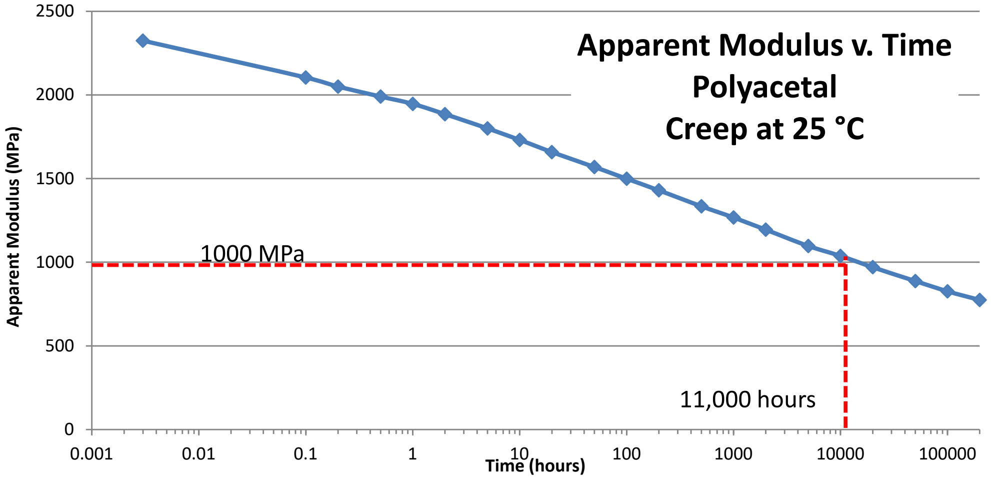


Starting Placement

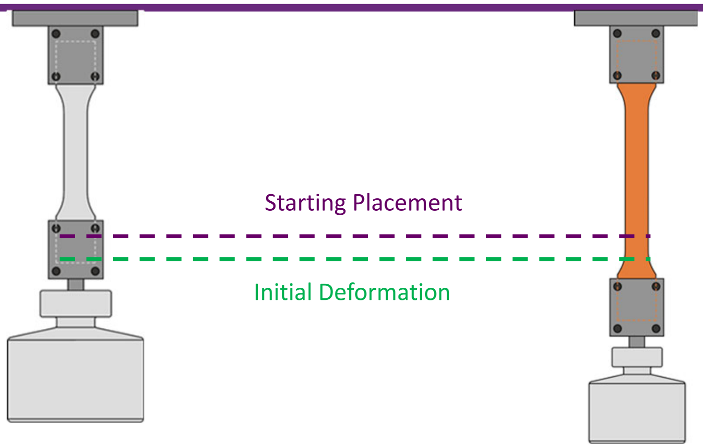
Initial Deformation

Day 100

Time Under Load

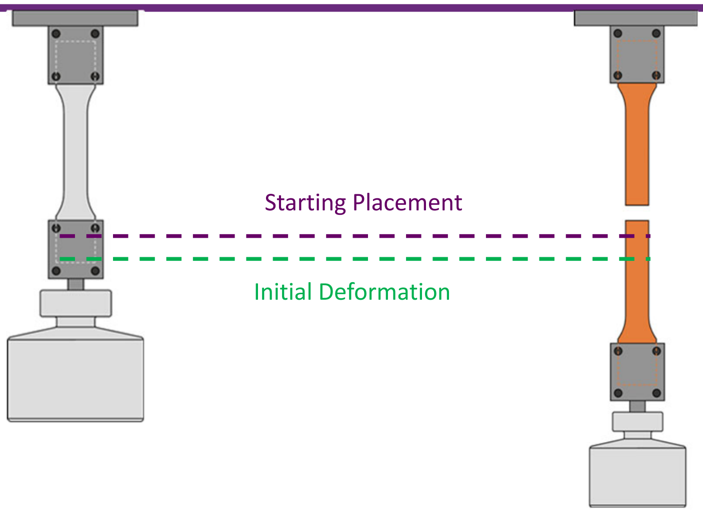


Time Under Load



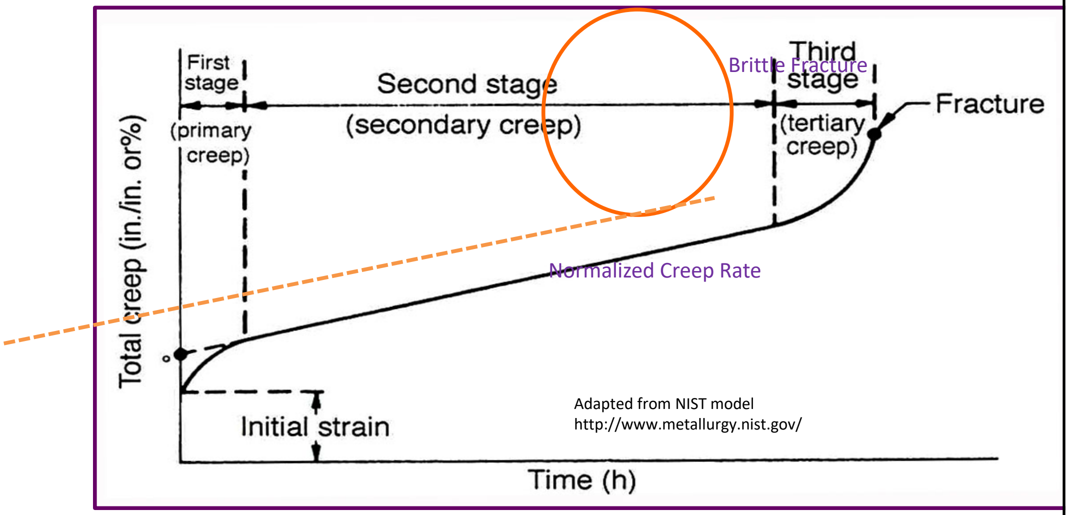
Day 100

Time Under Load

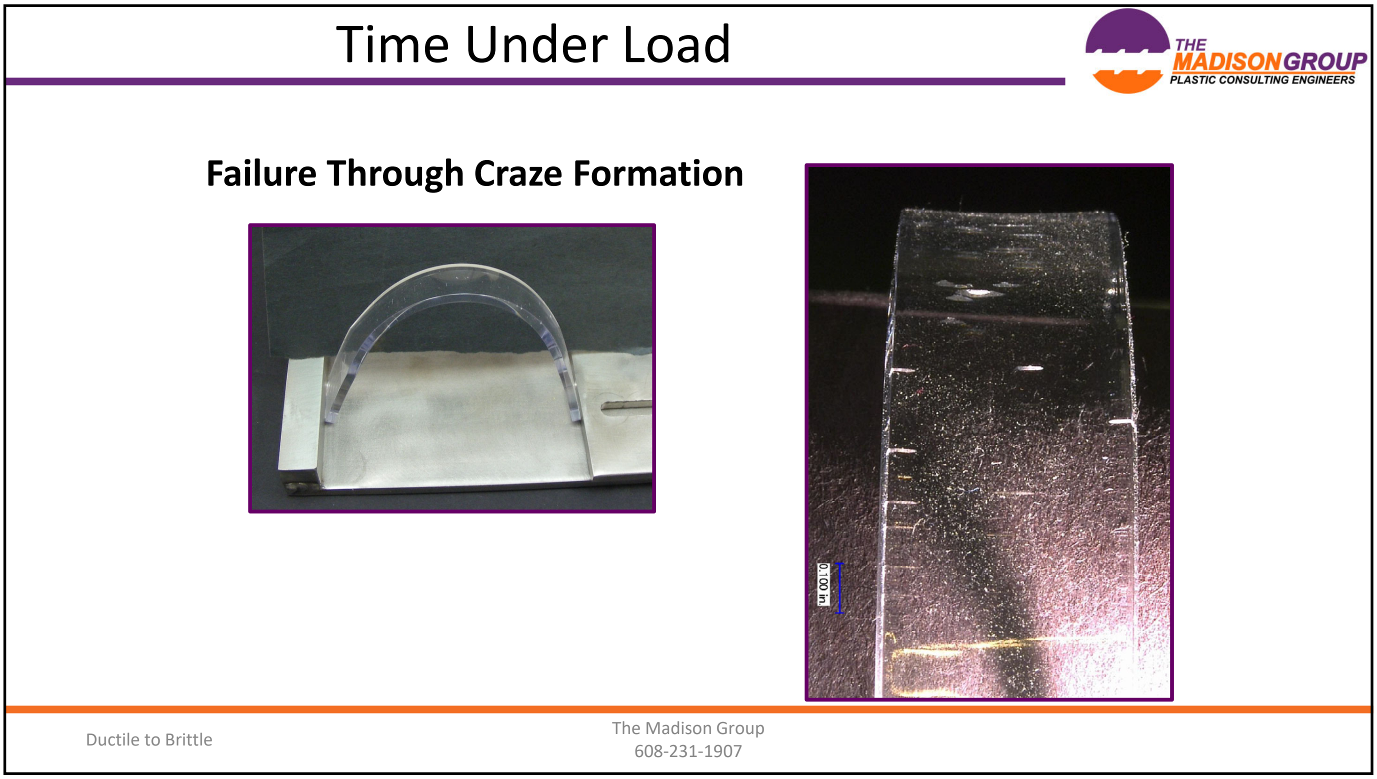


Day 1000?

Time Under Load

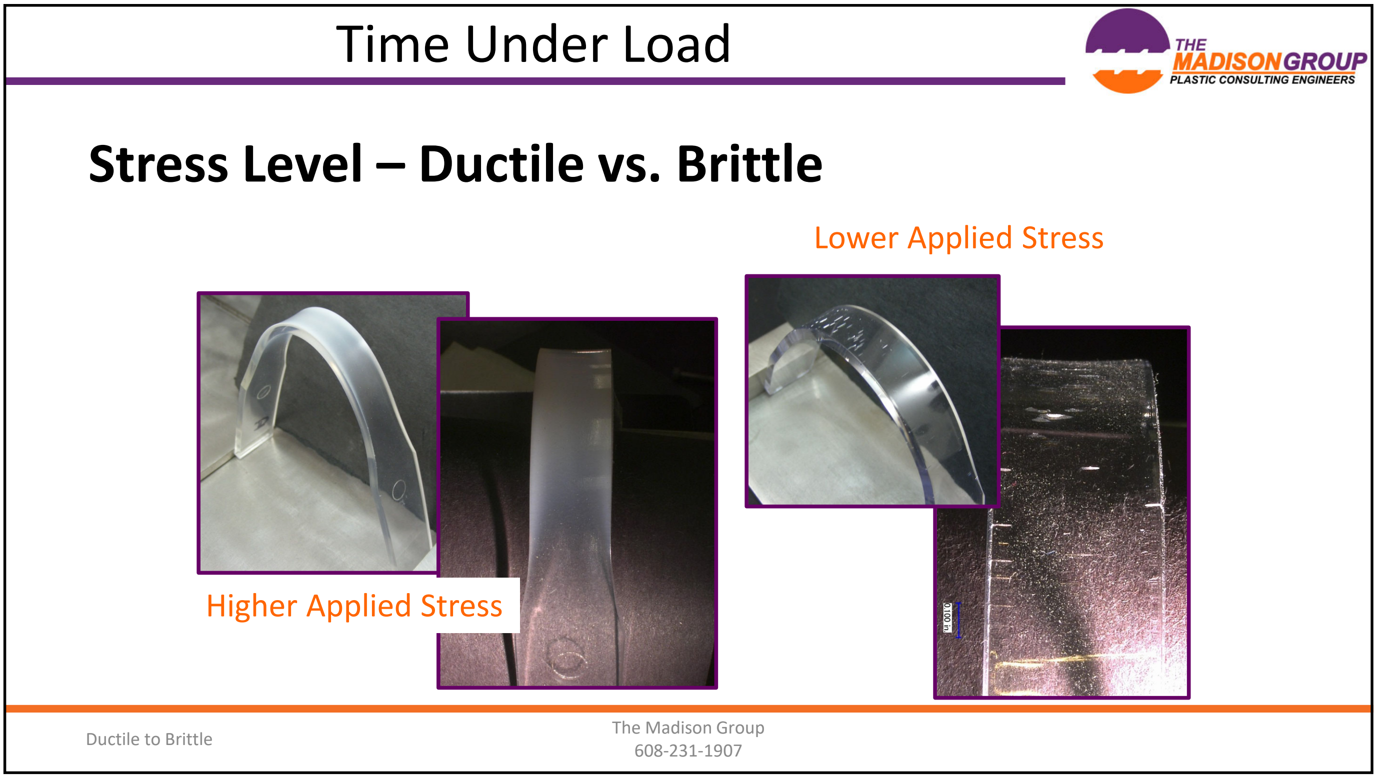


Adapted from NIST model
http://www.metallurgy.nist.gov/



Time Under Load

Failure Through Craze Formation



Time Under Load

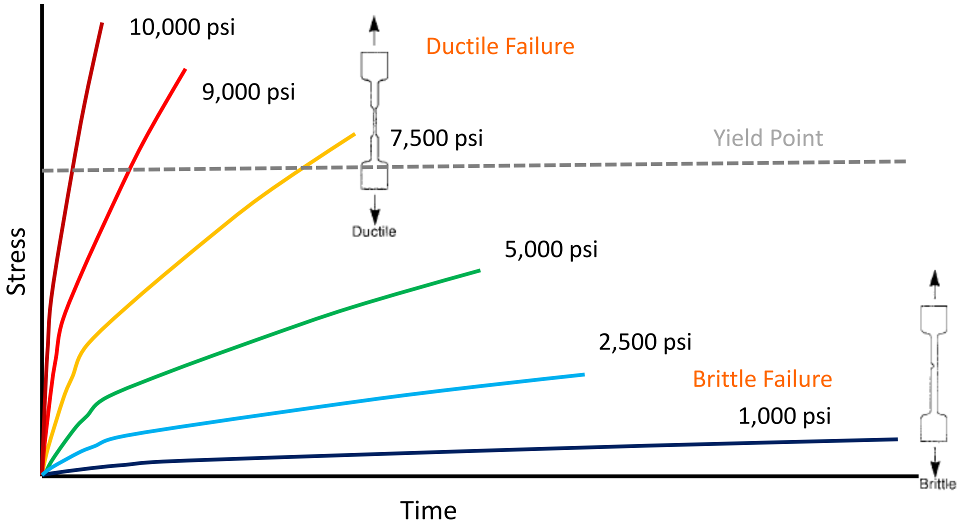
Stress Level – Ductile vs. Brittle

Lower Applied Stress

Higher Applied Stress

Time Under Load

Source: "Understanding the Consequence of Ductile-to-Brittle Transitions in a Plastics Materials Failure", Published and Presented at ANTEC, 2008



CHEMICAL CONTACT
ENVIRONMENTAL STRESS CRACKING

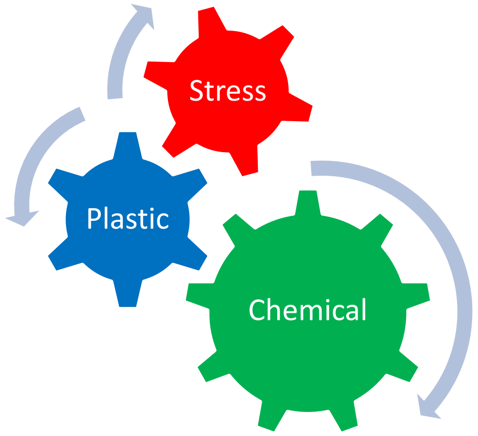
Chemical Contact - ESC

Environmental Stress Cracking is…

the premature embrittlement and subsequent cracking of a plastic due to the simultaneous and synergistic action of stress and contact with a chemical agent

Chemical Contact - ESC

Environmental Stress Cracking



Chemical Contact - ESC

Environmental Stress Cracking

- No chemical reaction between the polymer and the chemical agent
- No molecular degradation
- The plastic would undergo stress cracking in air given sufficient time
- The chemical accelerates the stress cracking

Chemical Contact - ESC

Environmental Stress Cracking

- Chemical agent permeates into molecular structure → lower ductility
- Mechanism includes interference with inter-molecular forces bonding polymer chains
- Reduces the energy required for disentanglement/slippage to occur producing a shift in the preferred mechanism from yielding

Chemical Contact - ESC

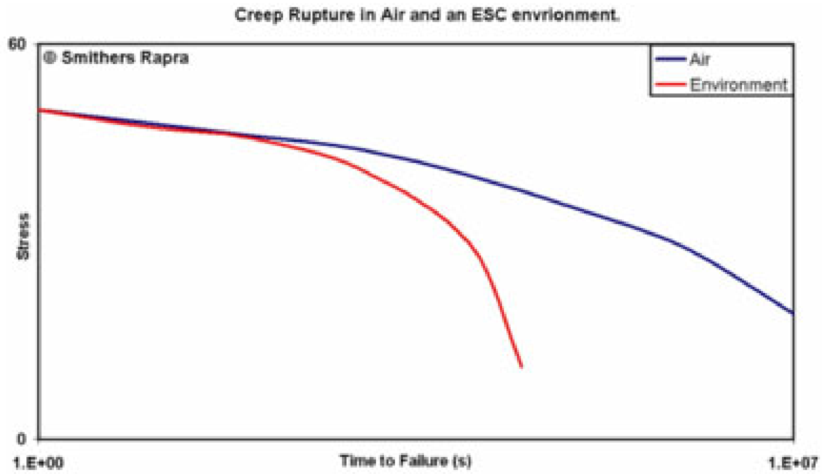
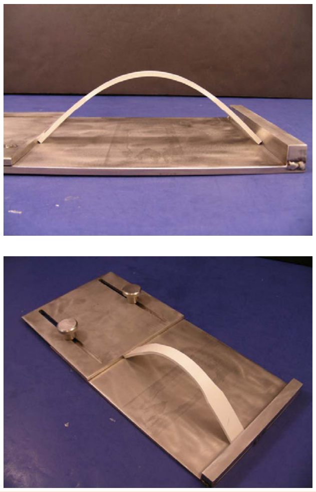
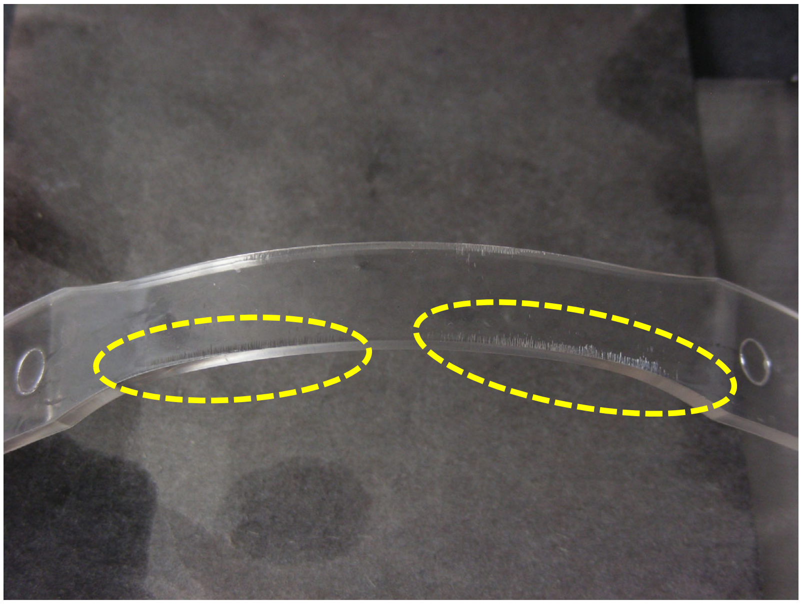


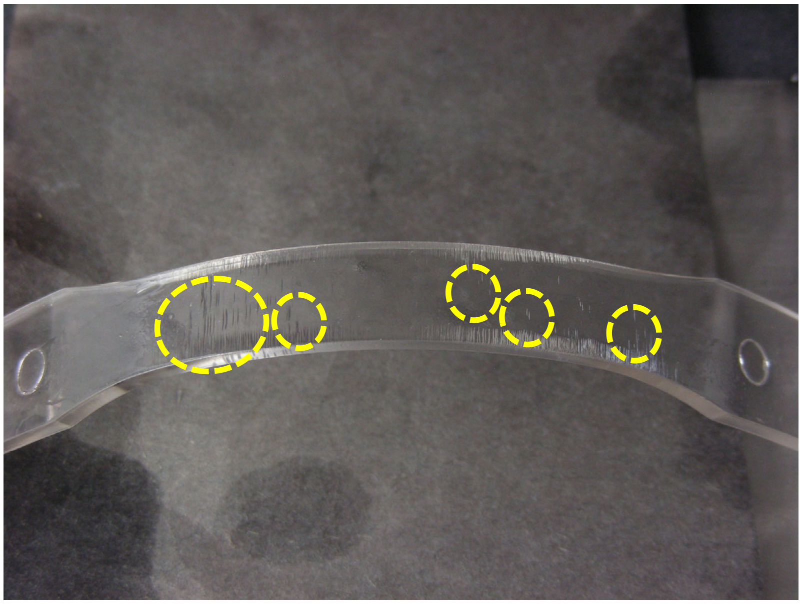
Diagram from Smithers RAPRA
http://www.rapra.net

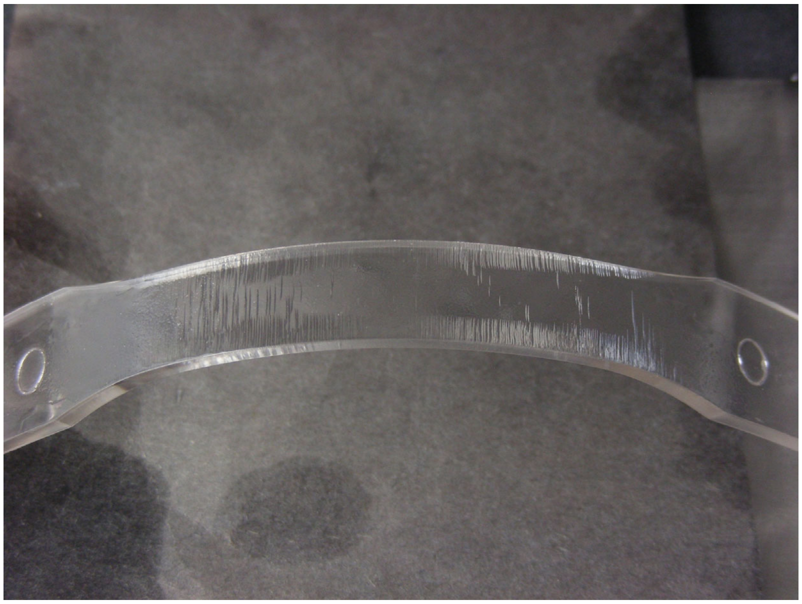
Chemical Contact - ESC

- Bent Strip Test
- ASTM D 543 Practice B – Mechanical Stress / Reagent Exposure
- Chemical Contract While Under Stress
- Inspection for Crack Formation









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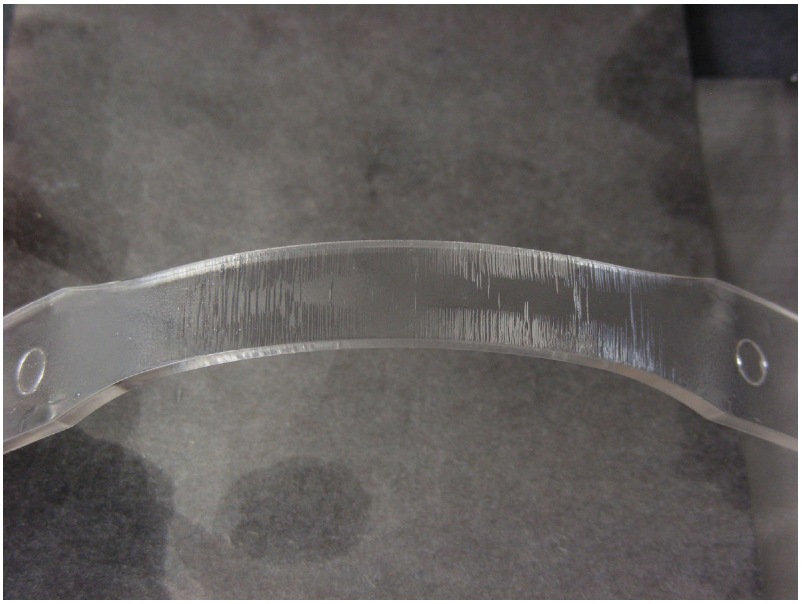

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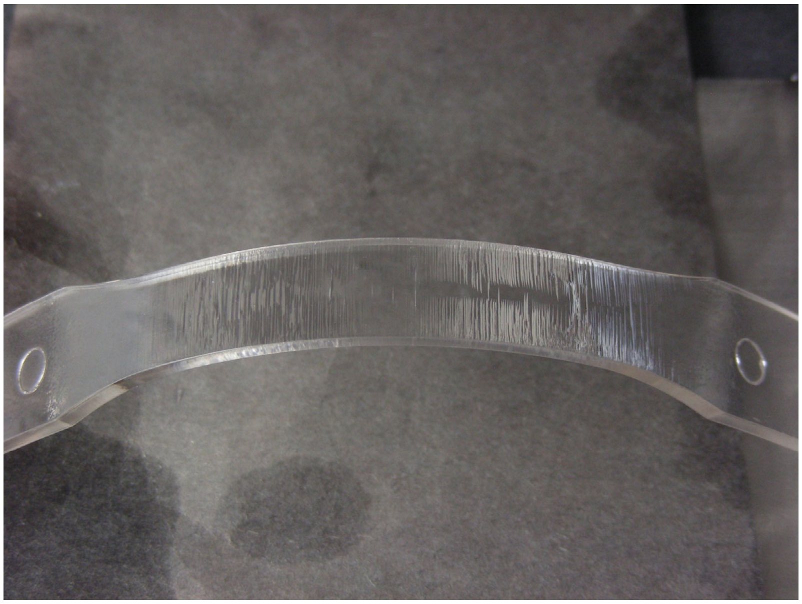
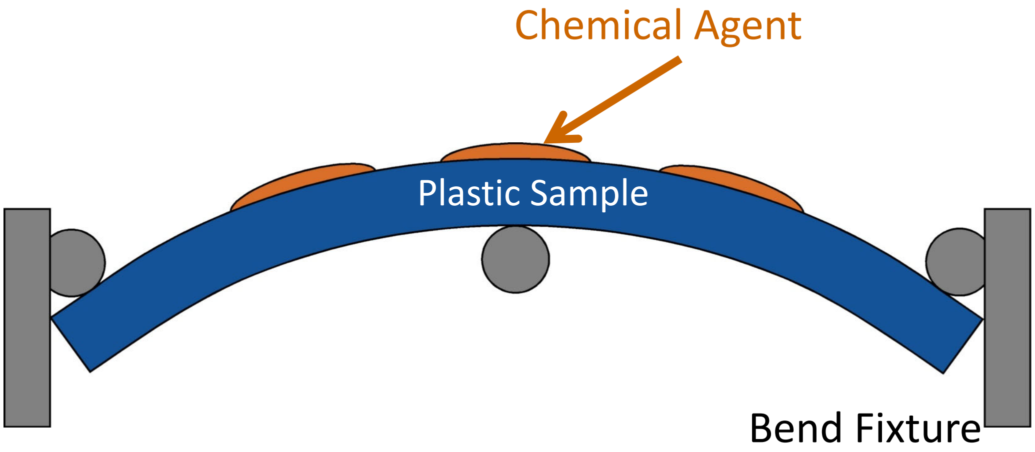
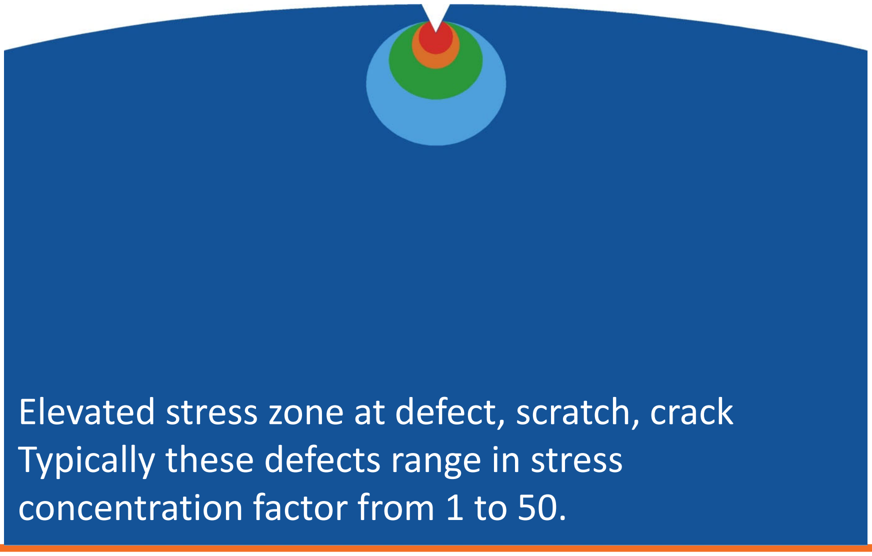


ESC Failure Mechanism

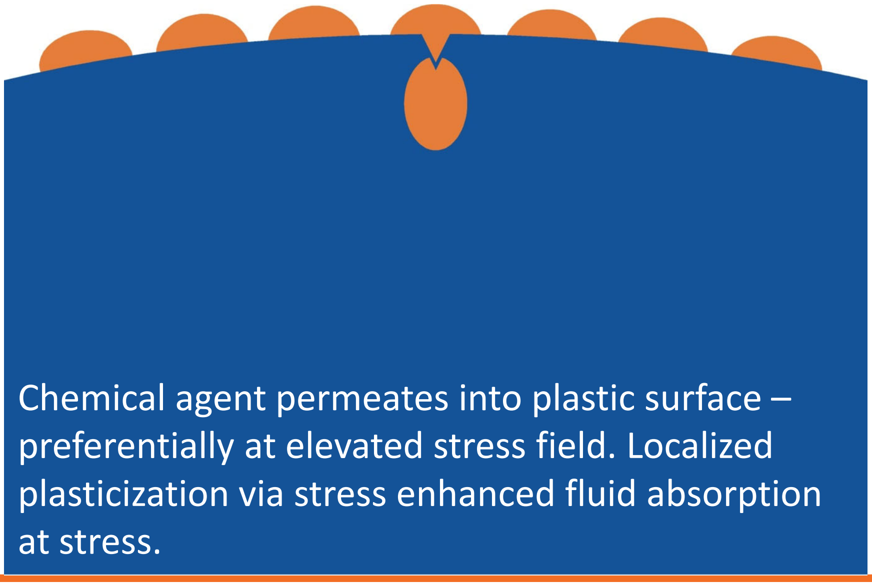


ESC Failure Mechanism



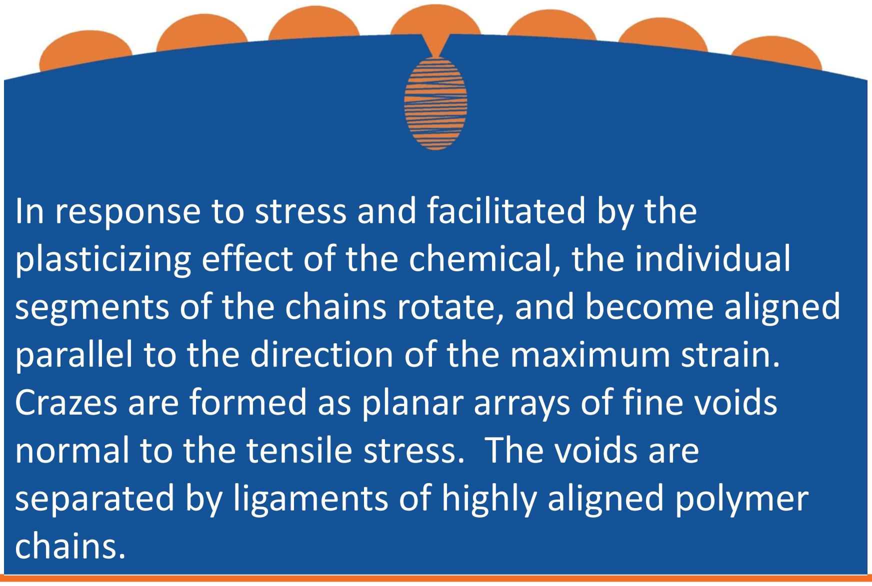
Elevated stress zone at defect, scratch, crack
Typically these defects range in stress concentration factor from 1 to 50.

ESC Failure Mechanism



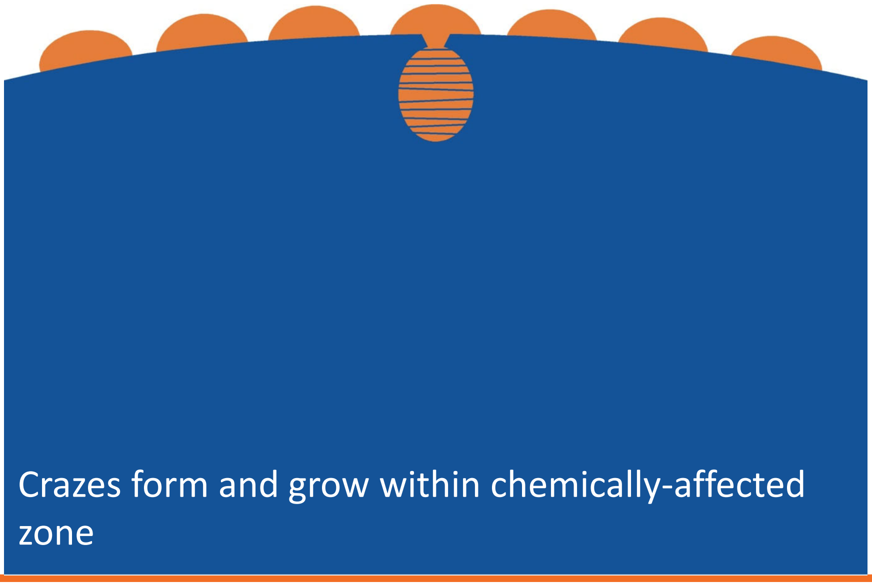
Chemical agent permeates into plastic surface – preferentially at elevated stress field. Localized plasticization via stress enhanced fluid absorption at stress.

ESC Failure Mechanism

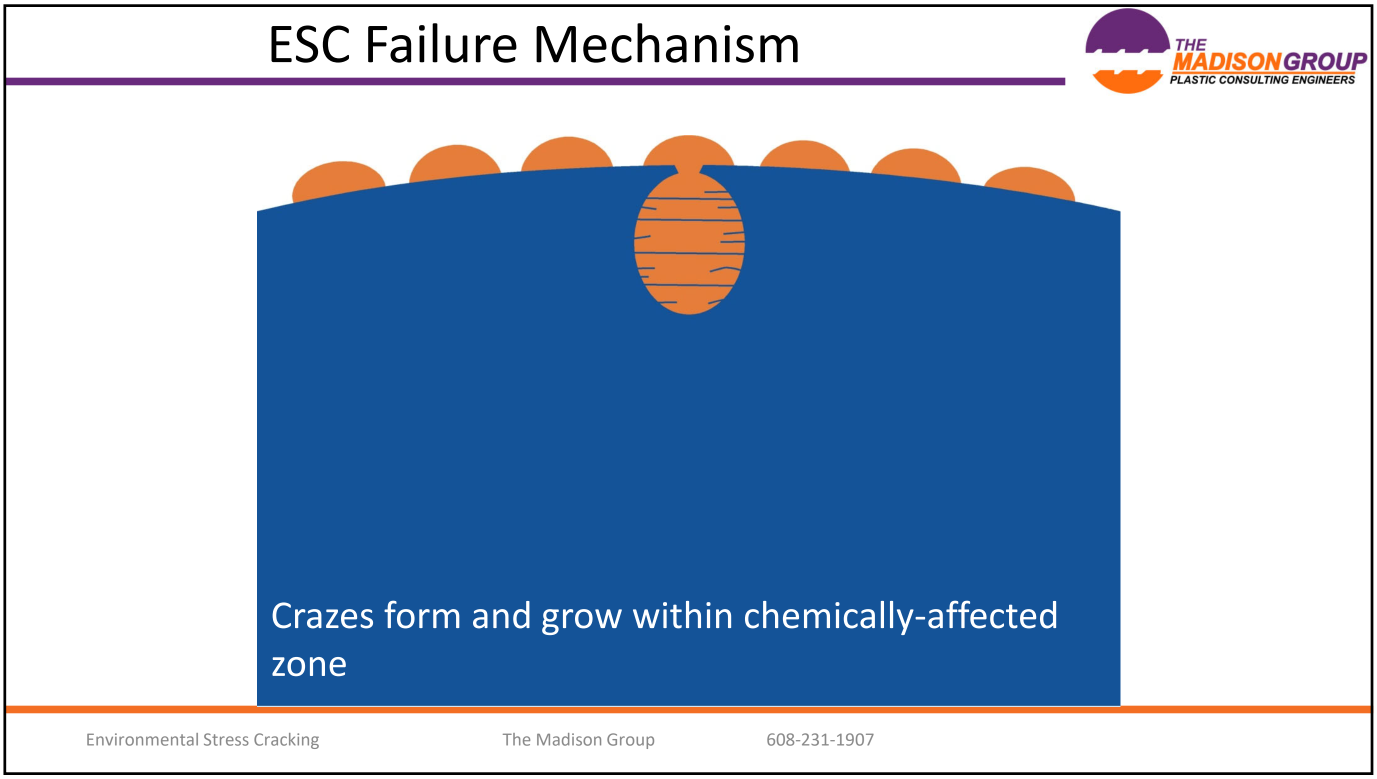


In response to stress and facilitated by the plasticizing effect of the chemical, the individual segments of the chains rotate, and become aligned parallel to the direction of the maximum strain. Crazes are formed as planar arrays of fine voids normal to the tensile stress. The voids are separated by ligaments of highly aligned polymer chains.

ESC Failure Mechanism

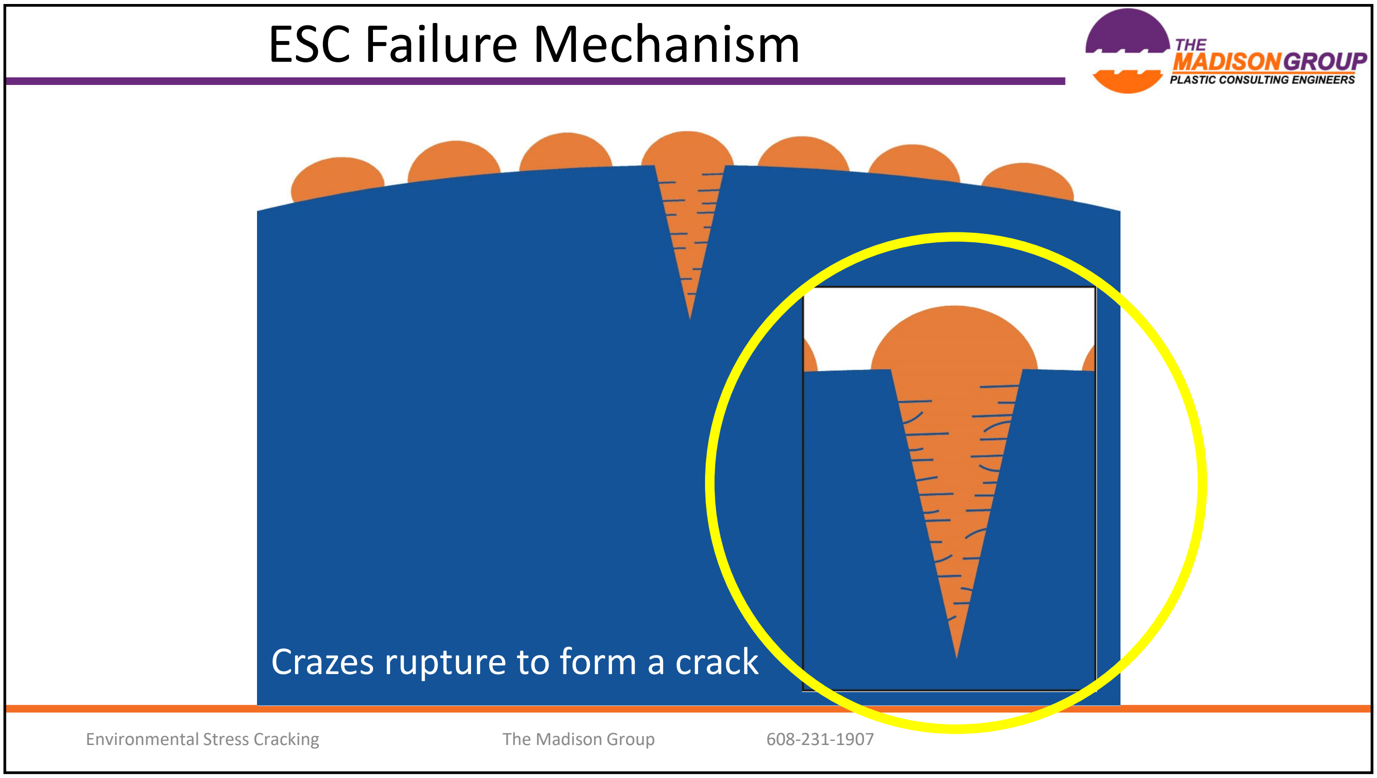


Crazes form and grow within chemically-affected zone



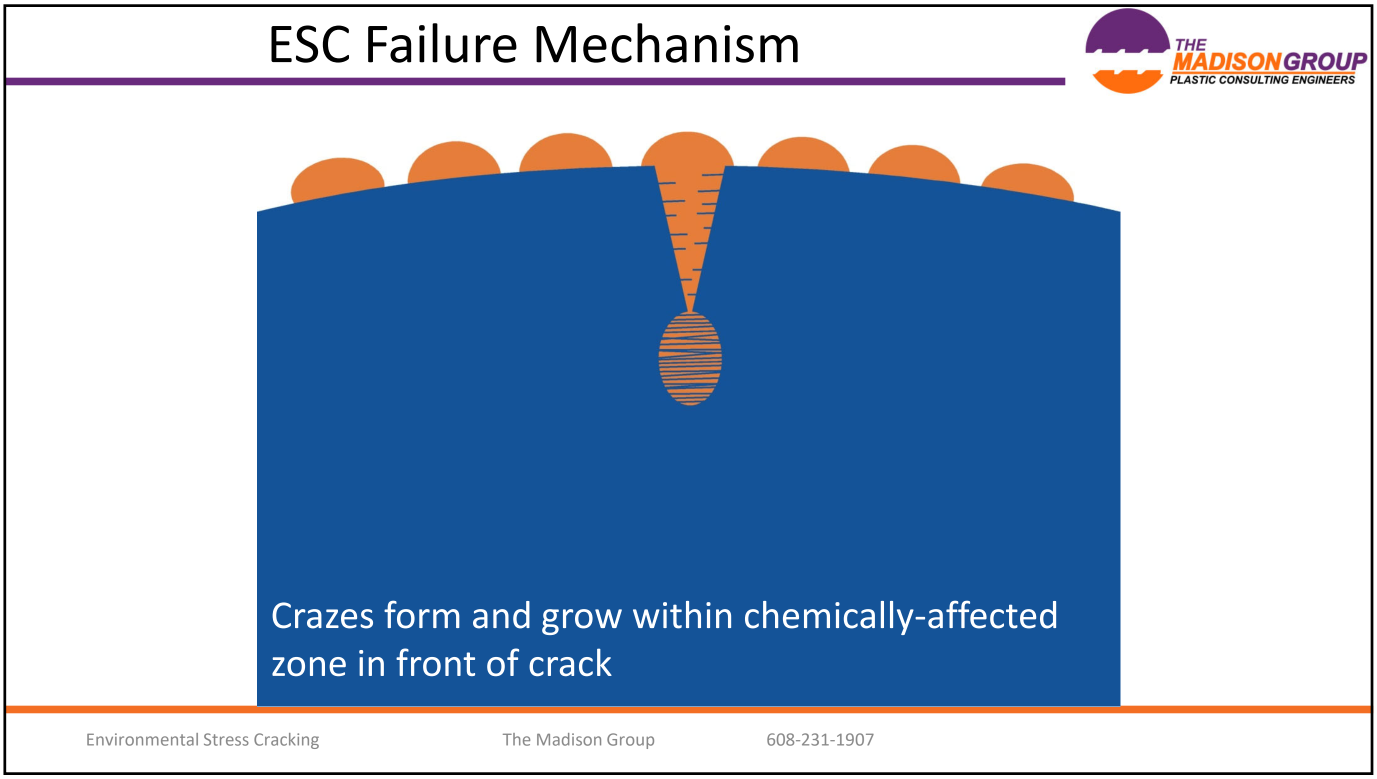
ESC Failure Mechanism

Crazes form and grow within chemically-affected zone



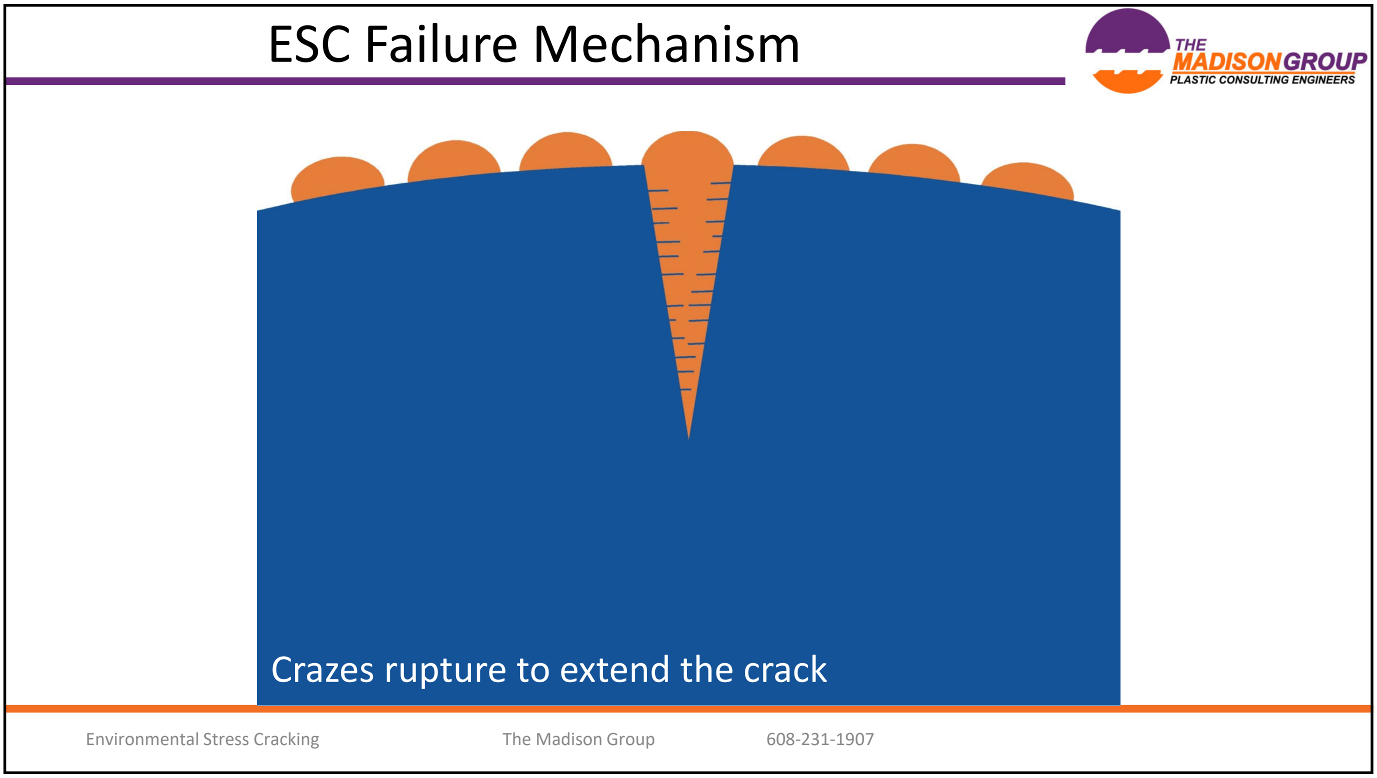
ESC Failure Mechanism

Crazes rupture to form a crack



ESC Failure Mechanism

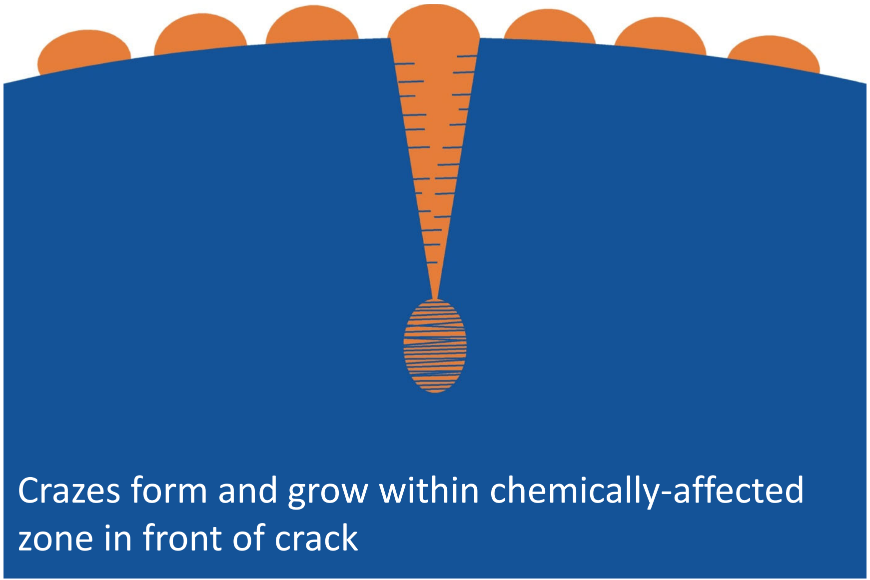
Crazes form and grow within chemically-affected zone in front of crack



ESC Failure Mechanism

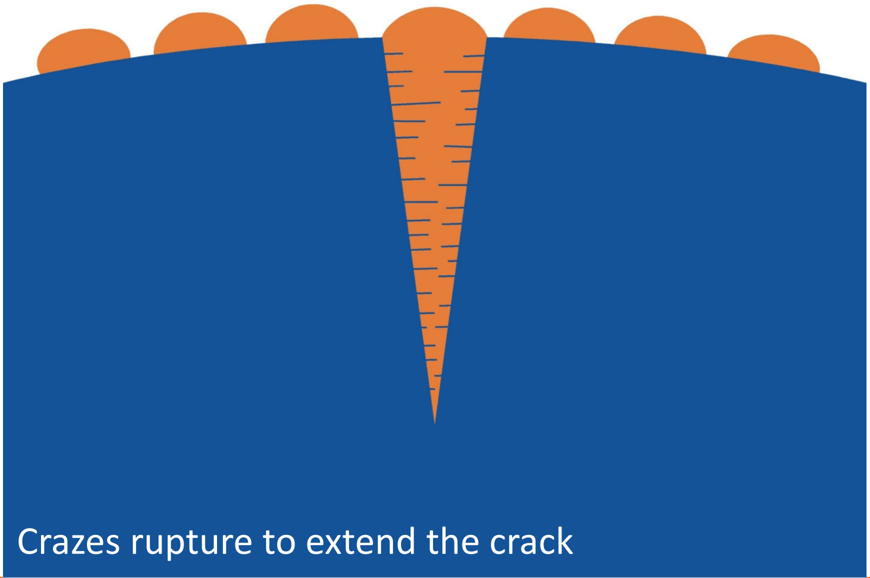
Crazes rupture to extend the crack

ESC Failure Mechanism



Crazes form and grow within chemically-affected zone in front of crack

ESC Failure Mechanism



Crazes rupture to extend the crack

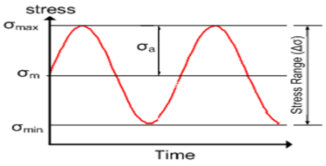
DYNAMIC STRESS

Dynamic Stress

Fatigue is….

“the progressive and localized structural damage that occurs when a material is subjected to cyclic loading. The nominal maximum stress values are less than the yield strength and tensile strength of the material”

Like creep, fatigue produces an apparent decay in strength.



Dynamic Stress

Fatigue:

The cyclic deformation of a plastic resulting from dynamic loading through stress or strain control

Dynamic Stress

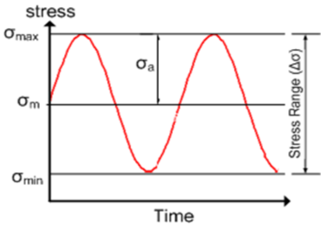
Fatigue

- Low to moderate forces exerted intermittently over an extended time → lower ductility. Can result in brittle fracture in normally ductile plastics
- Cyclic stress application leads to a decay in apparent modulus through localized molecular reorganization of polymer chains
- At stresses below the yield point molecular reorganization includes disentanglement as there is no opportunity for yielding

Dynamic Stress

Premise of fatigue is basic:

If a component is subjected to stress repeatedly, the material undergoes a decay in strength.



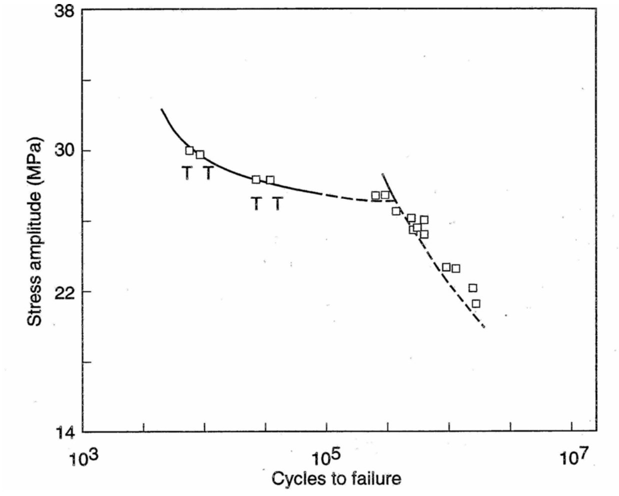
Dynamic Stress

Lexan 101 Polycarbonate

- Tensile Strength: 69 MPa
- Fatigue Strength: 59 MPa at 70,000 cycles
  45 MPa at 100,000 cycles
  31 MPa at 750,000 cycles
  7 MPa at 2,500,000 cycles

Dynamic Stress

Hysteresis vs. Brittle Fracture



Taken From "Fatigue of Engineering Plastics" by Hertzberg and Manson

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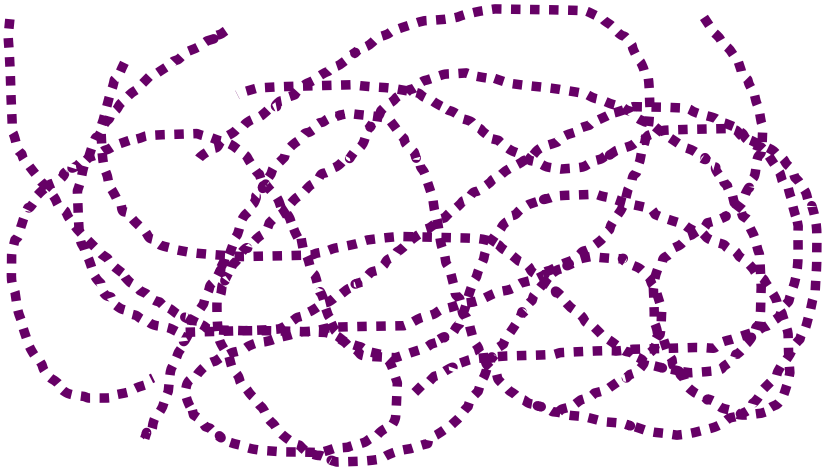
REDUCED MOLECULAR WEIGHT MATERIAL SELECTION

Molecular Weight

- Lower molecular weight → lower ductility
- Level of entanglement is different
- Reduces the energy required for disentanglement/slippage to occur – shifts preferred mechanism from yielding

Molecular Weight

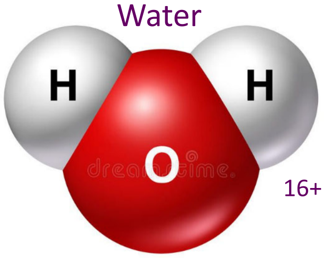


Multiple entangled chains made up of repeating units

Molecular Weight

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

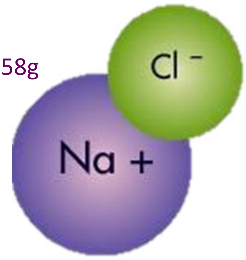
Water



16+1+1=18g

Sodium Chloride

23+35=58g

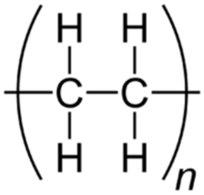


$6.02\ X10^{23}$ molecules / mole (molecular weight mass in grams)

Molecular Weight

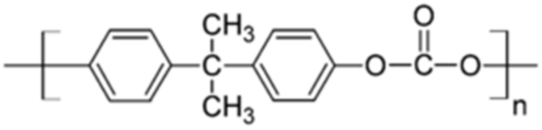
Molecular Weight: The sum of the atomic weights of the atoms in a molecule.

Polyethylene



(12x2 + 1x4) x n

Polycarbonate



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

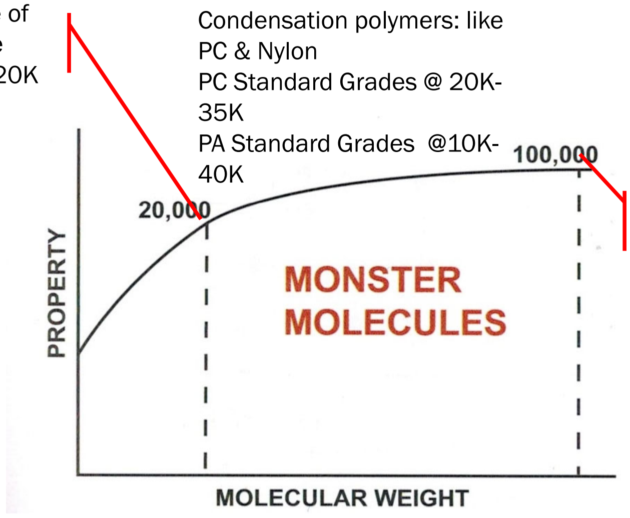
$6.02\ X10^{23}$ molecules / mole (molecular weight mass in grams)

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

Molecular Weight



Change of slope around 20K

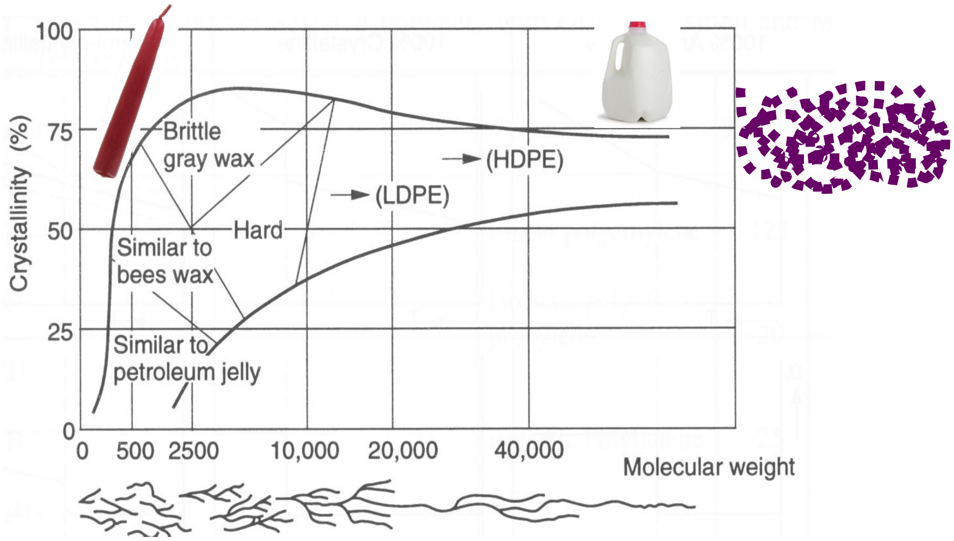
Condensation polymers: like PC & Nylon
PC Standard Grades @ 20K-35K
PA Standard Grades @10K-40K

Addition polymers like PS and PMMA

Ref: Ezrin, Plastics Failure Guide

Molecular Weight

THE MADISONGROUP
PLASTIC CONSULTING ENGINEERS



Molecular Weight

THE MADISONGROUP
PLASTIC CONSULTING ENGINEERS

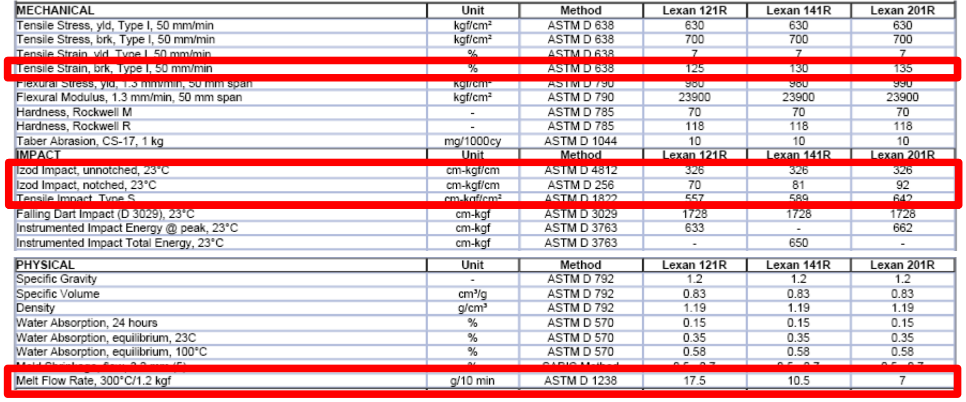
Selecting a Lower Molecular Weight Resin

Tensile Strength — Decreases ↓

- Tensile Strength
- Elongation at Break
- Yield Strength
- Impact Resistance
- Toughness
- Hardness
- Abrasion Resistance
- Thermomechanical Stability
- Chemical Resistance
- Creep and Fatigue Resistance

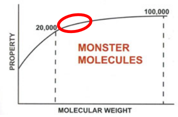
Molecular Weight

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**
Izod Impact, unnotched, 23°C	cm-kgf/cm	ASTM D 4812	326	326	326
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
Falling Dart Impact (D 3029), 23°C	cm-kgf	ASTM D 3029	1728	1728	1728
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
Mold Shrinkage, flow, 3.2 mm (5)	%	SABIC Method	0.5 - 0.7	0.5 - 0.7	0.5 - 0.7
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

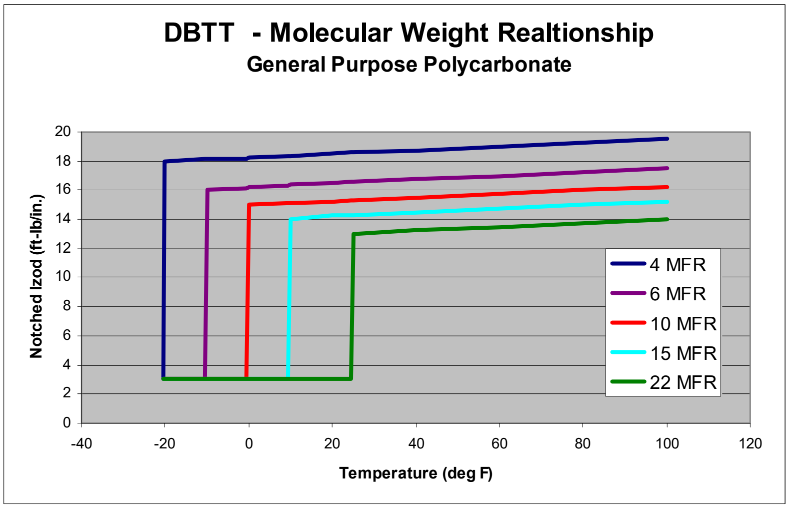
MFR (g/10min)	Fatigue Endurance Limit @ 10^7 Cycles (psi)
2.5	4000
9.0	3300
27.0	3000

Longer molecular chains produce a higher level of entanglement

Ref: Mike Sepe

Molecular Weight

DBTT vs. Molecular Weight



Source: Dow Plastics

MOLECULAR DEGRADATION

Molecular Degradation

Molecular Degradation Mechanisms

- Oxidation
- Hydrolysis
- Chain Scission
- Side Chain Alteration
- Destructive Crosslinking

Any point in the material life cycle

Molecular Weight Changes Permanently Through Chemical Reactions

Molecular Degradation

- 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

Molecular Degradation

Oxidation

Thermal oxidation is the chemical reaction of a polymeric material with oxygen from an oxidizing material, including air. The rate of the degradation reaction increases with increasing temperatures.

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

Molecular Degradation

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.

Molecular Degradation

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

MOLECULAR FUSION

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Molecular Fusion

- Less molecular entanglement → lower ductility
- Less intermolecular force to overcome disentanglement
- Knit lines and molecular orientation
- Molecular response shifts to disentanglement/slippage away from yielding because it requires less energy and with little entanglement opportunities for yielding are diminished

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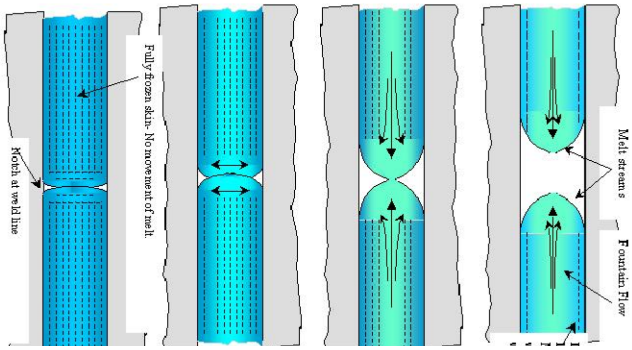
Molecular Fusion

Knit Lines

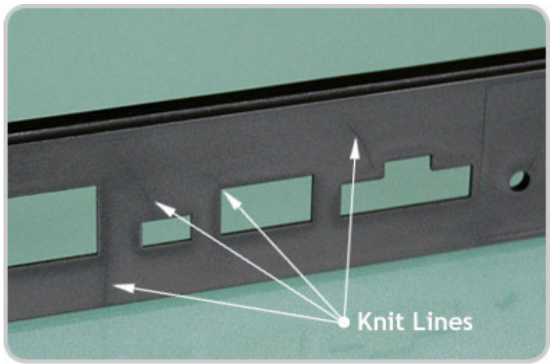
- Knit lines are areas in the molded part where two or more flow fronts converge.
- This area generally has lower strength than the other areas of the part.



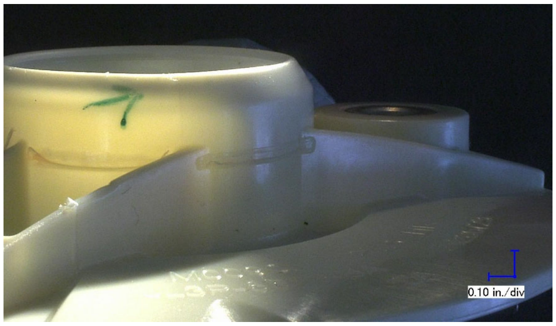
Molecular Fusion

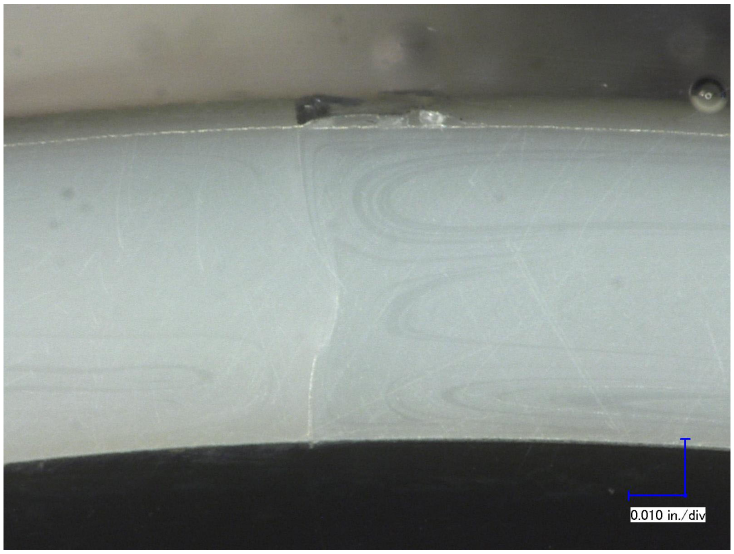
Knit Lines

Knit lines generally form on the opposite side of obstacles which are in the way of the normal flow path, such as pins that form holes in the part or bosses designed to accept inserts.



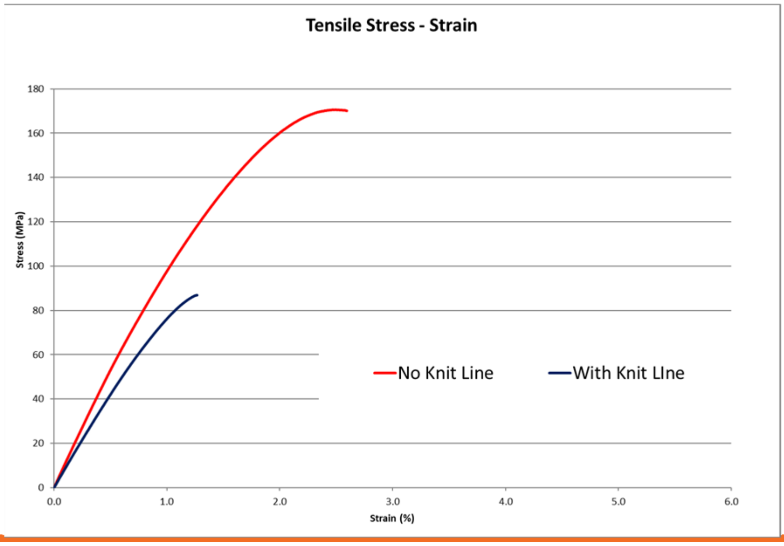
Molecular Fusion





Molecular Fusion

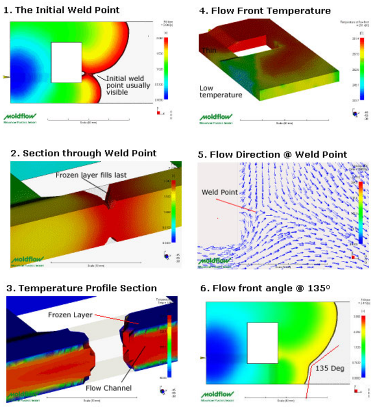
Knit Lines in Nylon 6 - Conditioned



Molecular Fusion

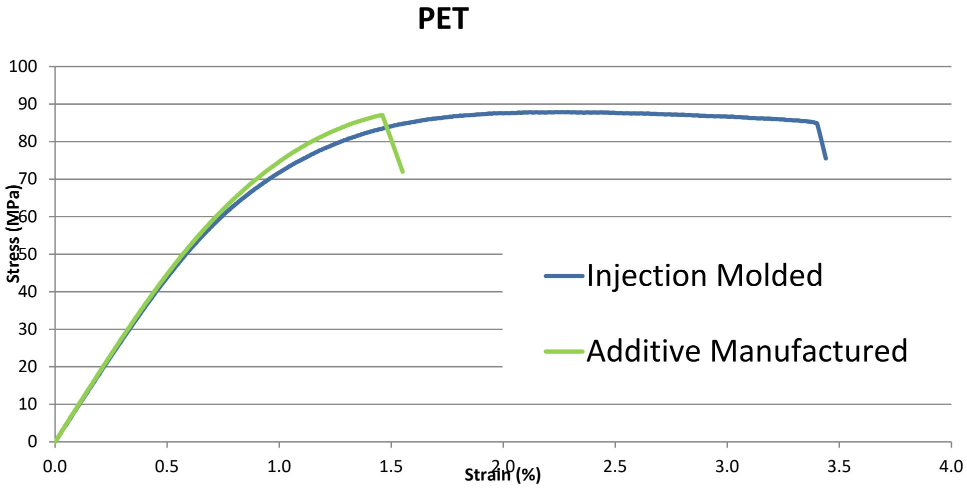
Knit Lines

Flow analysis programs can be used to anticipate knit lines, and direct them away from anticipated high stress areas of the part.



Molecular Fusion

Additive Manufacturing



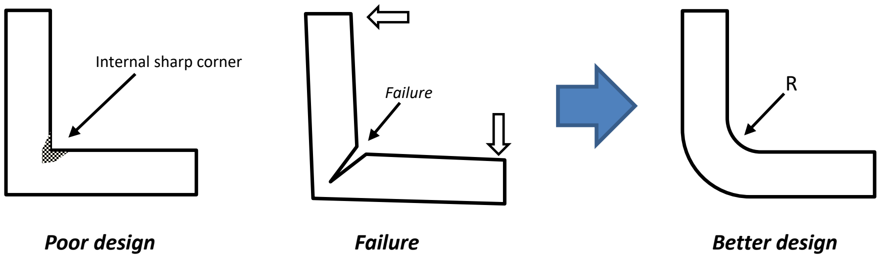
STRESS CONCENTRATION

Stress Concentration

- Higher levels of stress concentration → lower ductility
- Irregularities in a structure subjected to loading may produce high localized stress (stress concentration).
- These irregularities or stress risers include holes, sharp corners, notches, abrupt changes in wall thickness, or other geometric discontinuities.
- Notches or sharp corners introduce stress concentrations and can induce premature failures, especially during impact.

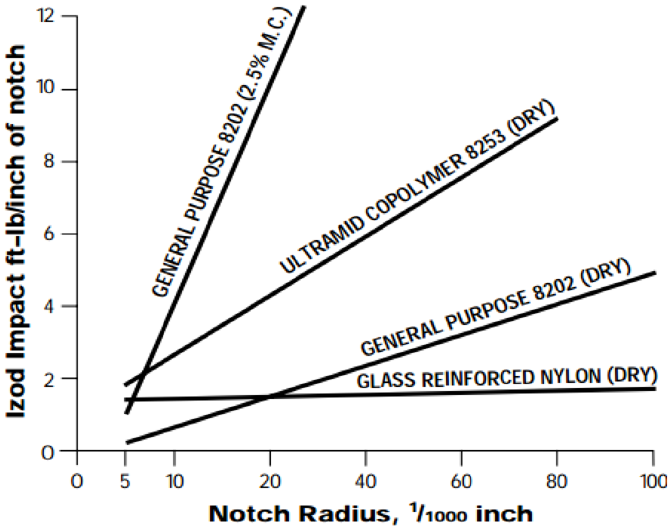
Stress Concentration

- The majority of plastics are notch sensitive and the increased stress at the notch is called the “Notch Effect”.
- Sharp corners results in stress concentration → lower ductility.

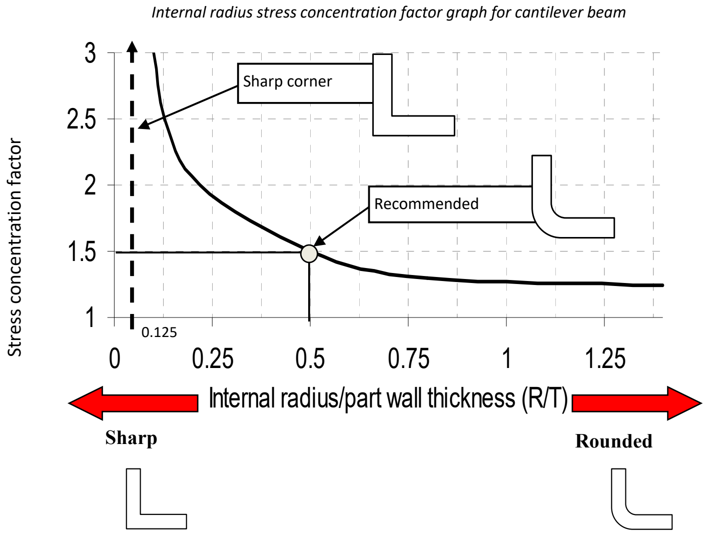


Stress Concentration

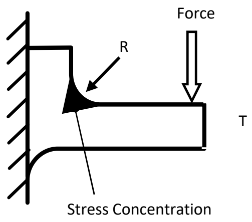
Notch Radii



Stress Concentration



Internal radius stress concentration factor graph for cantilever beam



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 Load
- Dynamic Stress Loading
- Chemical Exposure
- Loss of Plasticizer

- Molecular Degradation

Plastics Cracking

Plastic Ductile-to-Brittle Transitions

Production

- Low Molecular - Weight Material

Service

- Reduced Temperature

Disentanglement of Polymer Chains

- Molecular Degradation

- Molecular Degradation

Ductile-to- Brittle Transitions

BRITTLE		DUCTILE
lower	← Molecular Weight →	higher
broader	← Molecular Weight Distribution →	narrower
lower	← Temperature →	higher
higher	← Rate of Loading →	slower
higher	← Crystallinity →	lower
higher	← Filler Content →	lower
smaller	← Part Radius →	larger
abrupt	← Wall Thickness Transitions →	gradual
higher	← Internal Stresses →	lower
yes/varies	← Chemical Contact →	no/varies
less	← Plasticizer Content →	more
less	← Fusion →	more

Questions?

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