

Goals



- Gain an appreciation of the criticality of Molecular Weight on the performance of polymeric materials
- Get insight as to how Molecular Weight can be altered during life cycle of the polymer
- Identify different analytical tools to measure Molecular Weight, and recognize which is best in different circumstances

Molecular Weight

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Agenda

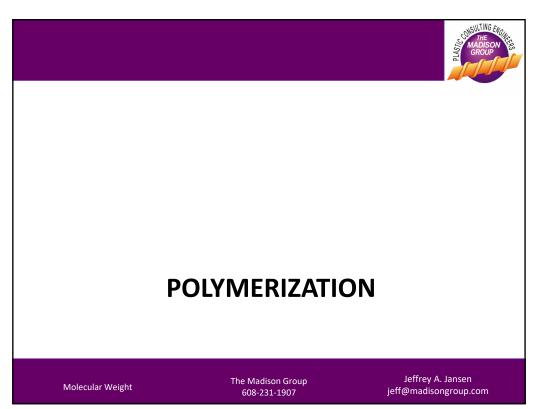


- Polymerization
- Molecular Weight and Its Relationship with Plastic Properties
- Chain Entanglement
- Molecular Weight Distribution
- Molecular Weight Measurement
- Molecular Degradation
- Complementary Methods for Assessing Molecular Degradation

Molecular Weight

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3



Plastic Properties



Molecular Structure

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

Material Composition

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

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5

Polymerization



Addition Polymerization

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

Exothermic Reaction

Molecular Weight

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Addition Polymerization

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

Exothermic Reaction

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7

Polymerization



Addition Polymerization

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

$$\begin{array}{c|c}
H & H \\
C = C \\
H & H
\end{array}$$
heat
pressure
catalyst
$$\begin{array}{c}
C - C \\
H & H
\end{array}$$
Ethylene monomer
$$\begin{array}{c}
\text{heat} \\
\text{pressure} \\
\text{catalyst}
\end{array}$$
Polyethylene

Exothermic Reaction

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Addition Polymerization

Polyethylene:

Free radical addition reaction

Chain initiation

The chain is initiated by free radicals, Ra•, produced by reaction between some of the ethene and the oxygen initiator.

Chain propagation

Each time a free radical hits an ethene molecule a new longer free radical is formed.

Molecular Weight

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Polymerization



Addition Polymerization

- Free radicals are used in extending the polymerization reaction.
- Because of that, addition polymers are highly susceptible to degradation mechanisms initiated by free radicals – oxidation, UV degradation.

Polyethylene Degradation Products Free Radicals Polyethylene

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Condensation Polymerization

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

$$n$$
 HO-CH₂CH₂-OH + n HO₂C \longrightarrow CO₂H

Endothermic Reaction

Molecular Weight

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11

Polymerization



Condensation Polymerization

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

$$n$$
 HO-CH₂CH₂-OH + n HO₂C \longrightarrow CO₂H

Endothermic Reaction

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Condensation Polymerization

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

$$\begin{bmatrix}
O & O \\
\parallel & \parallel \\
-NH(CH_2)_6NH-C(CH_2)_4C - \frac{1}{3}_n + 2nH_2O
\end{bmatrix}$$
Nylon 6,6

Endothermic Reaction

Molecular Weight

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13

Polymerization



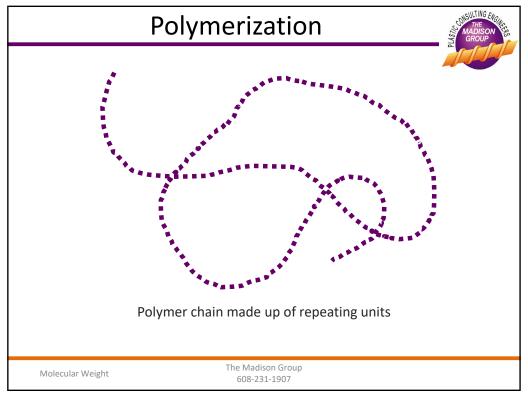
Condensation Polymerization

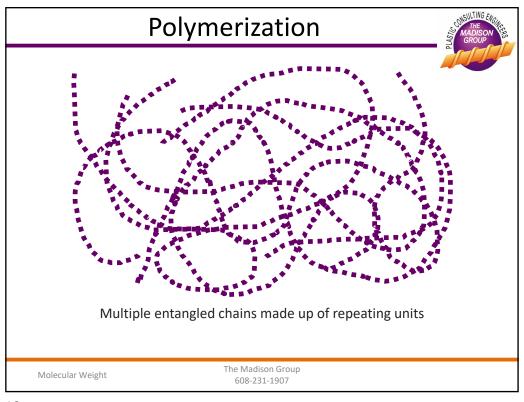
- Water is produced as a byproduct of polymerization.
- Because of that, condensation polymers are highly susceptible to hydrolysis.

$$n$$
 HO-CH₂CH₂-OH + n HO₂C \longrightarrow CO₂H

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MOLECULAR WEIGHT / PROPERTIES

Molecular Weight

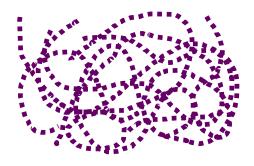
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17

Molecular Weight



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





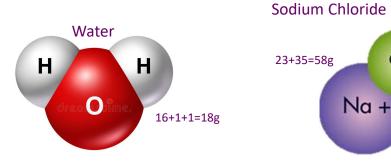
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Molecular Weight



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



6.02 X10²³ molecules / mole (molecular weight mass in grams)

Molecular Weight

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19

Molecular Weight



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

Polyethylene
$$\begin{pmatrix} H & H \\ I & I \\ C - C \\ I & I \\ H & H \end{pmatrix}_n$$

$$- \begin{bmatrix} CH_3 \\ CH_3 \end{bmatrix} - O - C - O \end{bmatrix}_n$$

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

Polycarbonate

(12x2 + 1x4) x n

6.02 X10²³ molecules / mole (molecular weight mass in grams)

Molecular Weight

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Molecular Weight



Water 1 mole = 18 grams

Sodium Chloride 1 mole = 58 grams Polyethylene 1 mole = ~500 lbs.

Polycarbonate 1 mole = \sim 50 lbs.

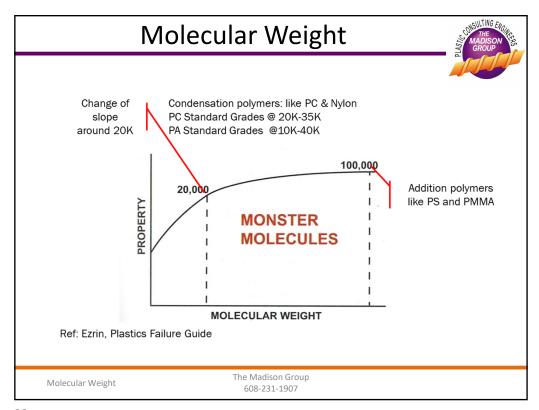
Most commercial polymers have an average molecular weight between 10,000 and 500,000

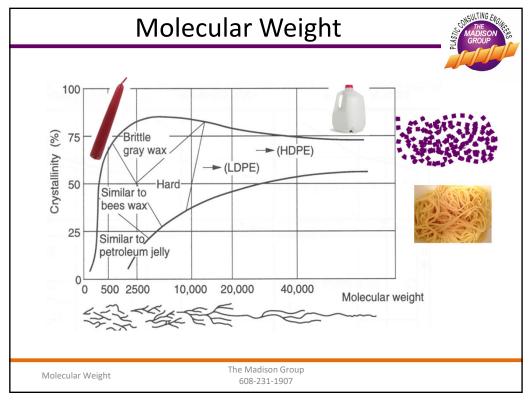
6.02 X10²³ molecules / mole (molecular weight mass in grams)

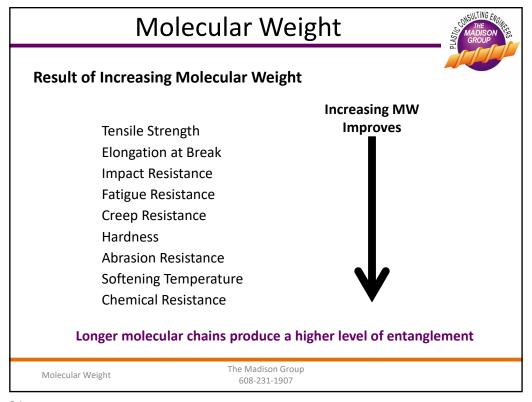
Molecular Weight

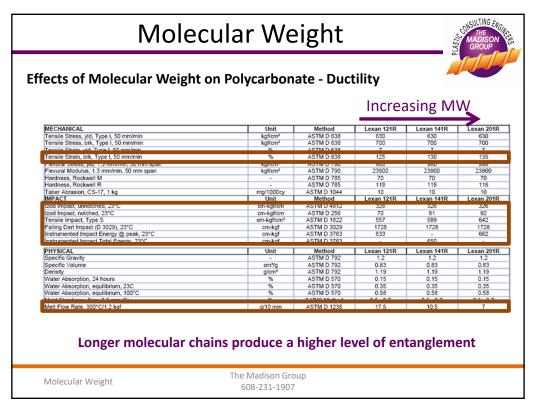
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21









Molecular Weight



Effects of Molecular Weight on the Impact Properties of Acetal Copolymer

MFR (g/10min)	Notched Izod (ft-lb/in)	Un-notched 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		

Ref: Mike Sepe

Longer molecular chains produce a higher level of entanglement

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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			

Ref: Mike Sepe

Longer molecular chains produce a higher level of entanglement

Molecular Weight

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27

Molecular Weight



Effects of Molecular Weight on the ESCR of HDPE

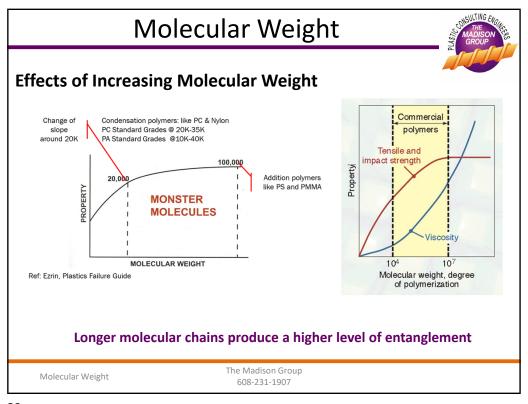
MFR (g/10min)	Time to ESC failure (hours)			
2	>1000			
4	375			
6	60			
8	10			
10	3			

Ref: Mike Sepe

Longer molecular chains produce a higher level of entanglement

Molecular Weight

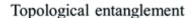
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Entanglement refers to the looping points produced in the polymer chain, or in between polymer chains, making the polymer chains unable to move normally and thus affecting the nature of the polymer.



Molecular Weight

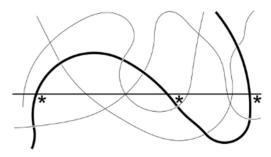
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31



The definition of entanglement is simple: if the chain crosses an arbitrary plane 3 times, then it is entangled.

This is real polymer physics, not just a simplistic guide.



https://www.stevenabbott.co.uk/practical-solubility/polymer-entanglement.php

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Entanglement of polymers is an important aspect to many of the properties of plastics.

If polymer chains are simply "intermingled" nothing much happens.

However, if the chains entangle, there alterations to the structure that influence mechanical and physical properties.

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33

Chain Entanglement



The level of entanglement is based on two primary factors

- The Stiffness of the polymer chain
- The Length of the polymer chain







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This is the same for polymer chains. A short and/or stiff polymer chain hardly tangles so it is easy to pull the chains. But long and/or flexible, they tangle and pulling them apart is difficult, giving high strength and ductility.







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Chain Entanglement



Mw is the weight average molecular weight of the polymer

<u>Me</u> is the average molecular weight between chain entanglements

<u>Mc</u> is the critical molecular weight – above this entanglements occur

The mechanical properties and the predominant mode of failure and the energy required to cause a specimen to fail, depend on the ratio Mw/Me.

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Polymer	Critical MWt			
PE	4,000			
PP	7,000			
PS	32,000			
PVOH	7,000			
PVA	25,000			
PMMA	18,000			
PC	4,500			

PMMA and PS have a high Mc. Both known for not being tough.

PC and PE have low Mc and are known for good ductility.

https://www.stevenabbott.co.uk/practical-solubility/polymer-entanglement.php

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37

Chain Entanglement



Processability is also dependent on the frequency of entanglements.

The more entangles the higher the melt viscosity – the more difficult to process.

Good Melt Processability, Poor Mechanical Properties

Optimum M_w Range

Good Mechanical Properties, Poor Melt Processability

M_w<10M_e

10M_e≤M_w≤15M_e

15M_e<M_w

 $M_w < 5M_e$

 $5M_e \le M_w \le 7.5M_e$

 $7.5M_e < M_w$

https://www.polymerexpert.biz/blog/131-optimum-molecular-weight-range-for-thermoplastics

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MOLECULAR WEIGHT DISTRIBUTION

Molecular Weight

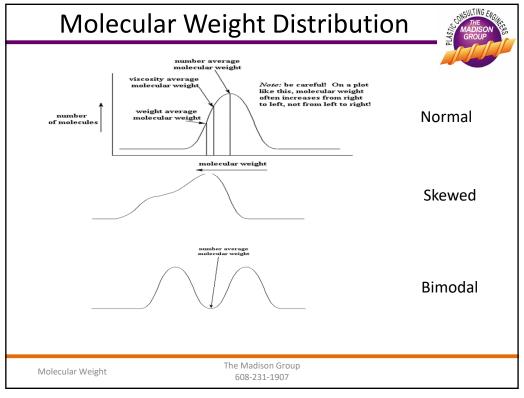
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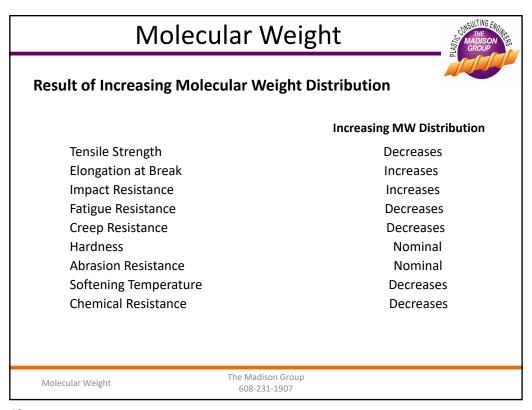
39

Molecular Weight Distribution



- Molecular Weight Distribution: The relative amounts of polymers of different molecular weights that comprise a given specimen of a polymer.
- Polymers are polydisperse they contain chains of unequal length.
- Polymers exist as a distribution of chain lengths and molecular weights.







MEASURING MOLECULAR WEIGHT

Molecular Weight

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43

Measuring Molecular Weight



Reasons to measure molecular weight

- Quality control of polymerized polymer to verify it meets specifications (Resin manufacturer)
- Quality control to verify compounding has not excessively degraded the plastic (Compounder)
- Incoming inspection to verify resin meets specifications (Molder)
- Quality control to verify molding process has not excessively degraded the plastic (Molder)
- To assess the potential for using regrind identify potential molecular weight reduction (Molder)
- Incoming inspection to verify molded part specifications (OEM)
- As part of a failure analysis (All)

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Measuring Molecular Weight



Molecular Weight Determination

Three Key Methods:

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

Molecular Weight

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45

Measuring Molecular Weight - GPC

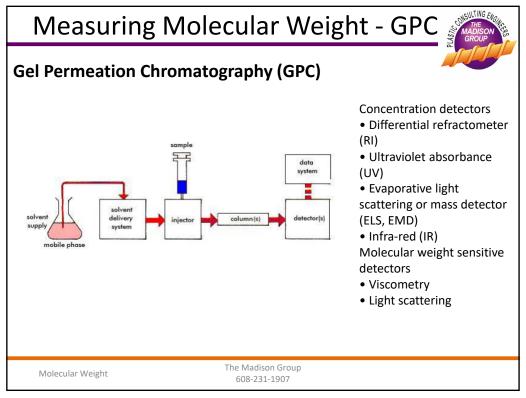


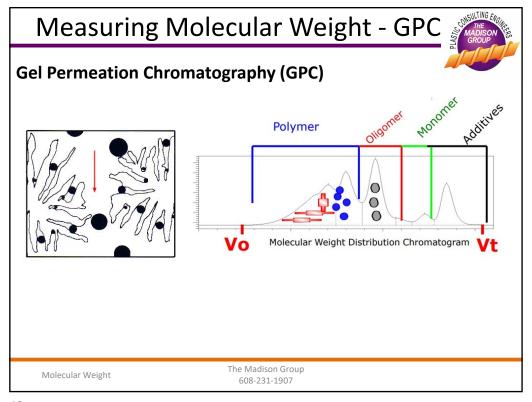
Gel Permeation Chromatography (GPC)

- GPC is a type of size exclusion chromatography based on liquid chromatography
- Separates analytes based on 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

Molecular Weight

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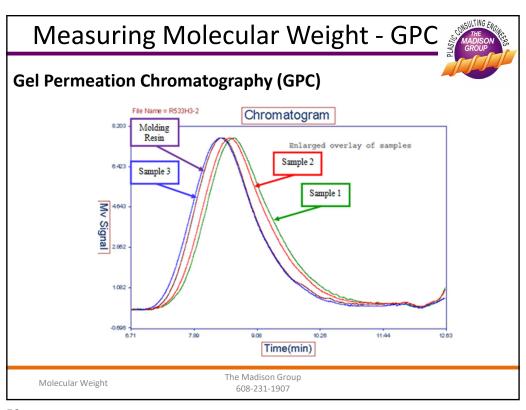
Measuring Molecular Weight - GPC Gel Permeation Chromatography (GPC) GPC is the only technique for characterizing polymer molecular weight distribution As molecular weight increases the strength and toughness of the polymer increases However as molecular weight increases the polymer becomes more difficult to process GPC provides key information to predict the processability and material properties of a polymer MWD determined by GPC

Log M

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49

Molecular Weight



Measuring Molecular Weight - GPC



Gel Permeation Chromatography Results (Average Molecular Weight)

Sample	Run	M _n		M_{w}		M _z		M _w /M _n	
Molding	1	9,702	0.750	46,512	16 556	84,961	85,207	4.79	4.77
Resin	2	9,816	9,759	46,601	46,556	85,093	65,207	4.75	4.77
Cample 1	1	1 9,003	0.005	33,926	33 881	64,318	64,261	3.77	3.73
Sample 1	2	9,167	9,085	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	

Molecular Weight

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51

Measuring Molecular Weight - GPC

Mn - number average molecular weight

Mw - weight average molecular weight

Mv - viscosity average molecular weight

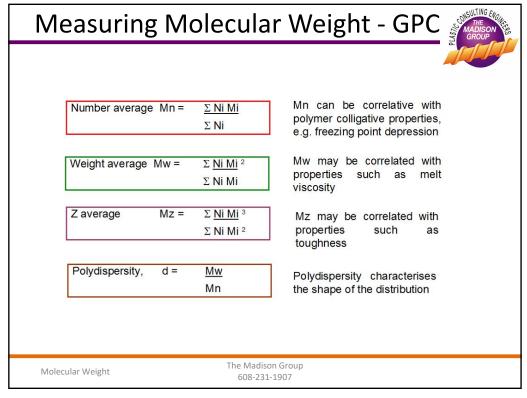
Mp - peak molecular weight

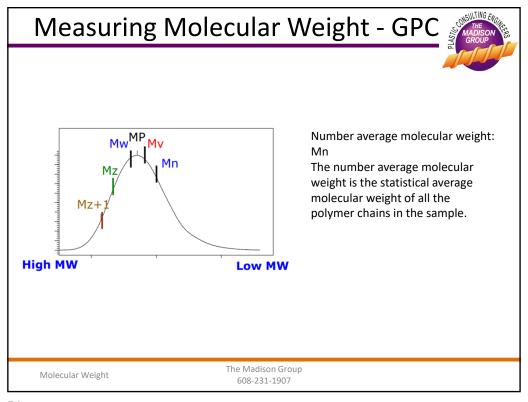
Mw/Mn - polydispersity by GPC

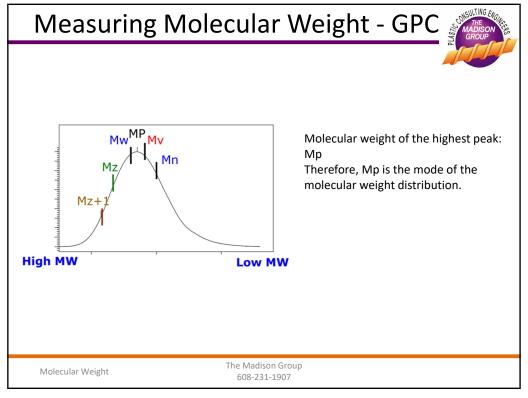
TENSILE STRENGTH **BRITTLENESS-FLOW HARDNESS PROPERTIES** $\overline{\mathbb{M}}_{\mathsf{W}}$ \bar{M}_n FLEX LIFE **EXTRUDABILITY STIFFNESS** MOLDING PROPERTIES

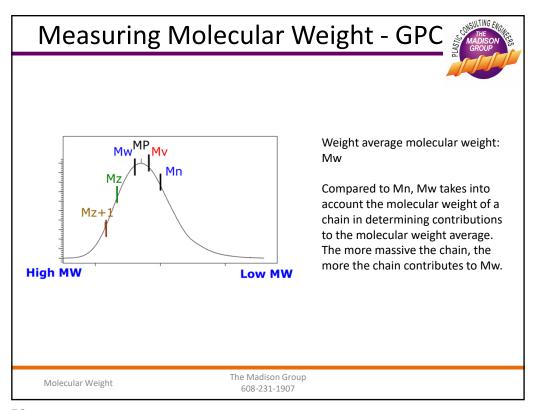
Molecular Weight

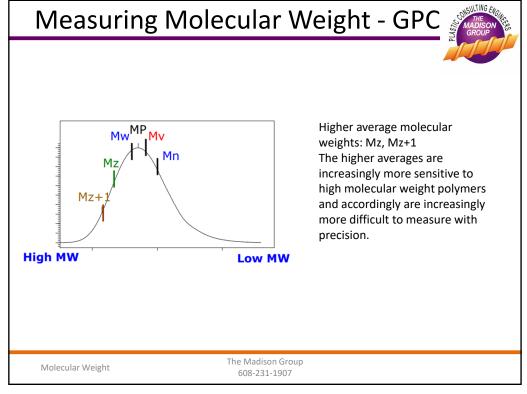
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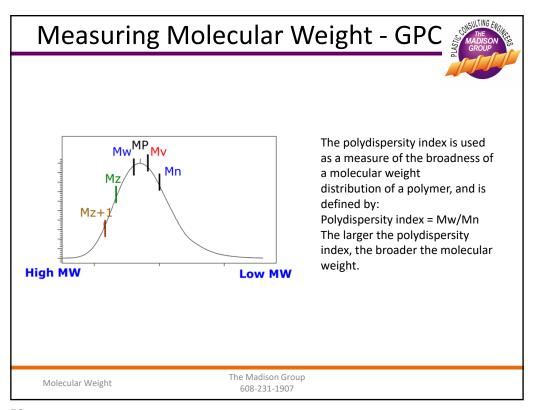


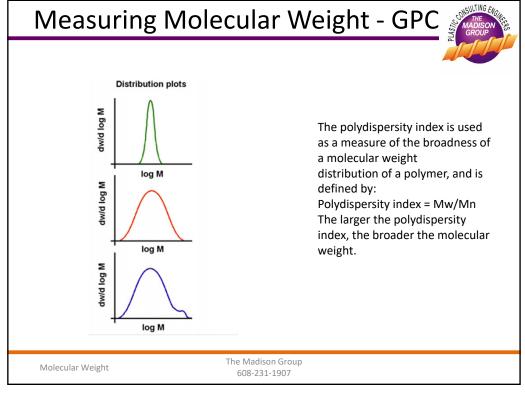












Measuring Molecular Weight - IV



Intrinsic Viscosity (IV)

- 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

Molecular Weight

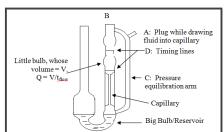
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Measuring Molecular Weight - IV



Intrinsic Viscosity (IV)

- 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



Molecular Weight

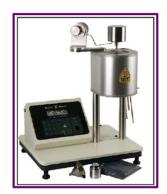
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61

Measuring Molecular Weight - MFR

Melt Flow Rate (MFR)

- 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.



Molecular Weight

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Measuring Molecular Weight - MFR



Melt Flow Rate (MFR)

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



 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
- Testing can be conducted at two conditions representing different shear rates (capillary rheology)
- Experiments can be run to assess thermal stability

Molecular Weight

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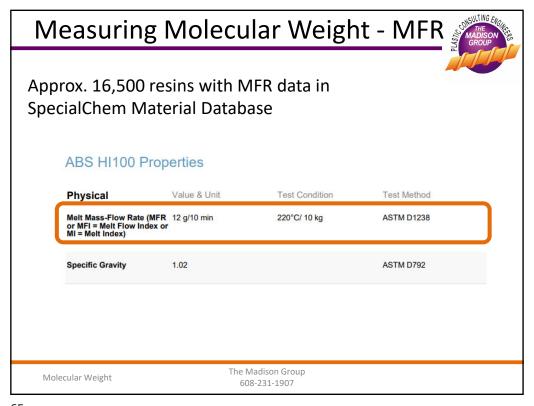
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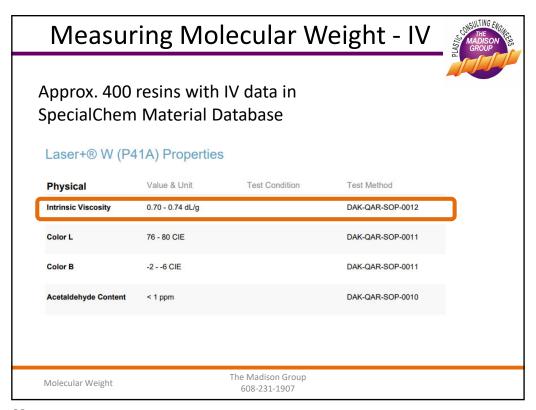


PICKING THE RIGHT TEST

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Measuring Molecular Weight - GPC



O resins with GPC or molecular weight data in SpecialChem Material Database



Molecular Weight

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67

Measuring Molecular Weight



In order to identify molecular degradation, a resin sample or previous data is required for GPC, and in most cases IV.

It is possible to compare MFR results with nominal datasheet value – not ideal

Molecular Weight

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Measuring Molecular Weight

MFR

Advantages

- · Data availability
- Ease of testing
- Low cost of contract testing
- Relatively low cost of equipment

Disadvantages

- Indirect measure of average molecular weight
- No molecular weigh distribution information
- Glass fiber reinforced results – confounded
- Nylon moisture content
- 15 g required
- · Sample drying
- · Sample cutting

IV

Advantages

- No interference from glass fibers
- Small sample size
- Moderate cost of contract testing
- Relatively low cost of equipment

Disadvantages

- · Lack of available data
- Resin required for comparisons
- Need accurate filler content
- · Solvents used in testing
- Need to dissolve sample

GPC Advantages

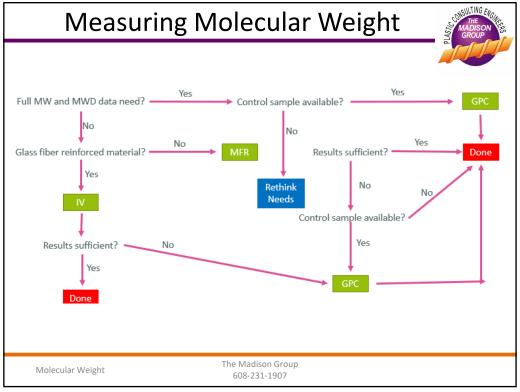
- Absolute molecular weight values
- Molecular weight distribution results
- · Small sample size

Disadvantages

- Sophistication of test procedure
- Solvents used in testing
- Need to dissolve sample
- High cost of contract testing
- High cost of equipment

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MOLECULAR DEGRADATION

Molecular Weight

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71

Molecular Degradation



Molecular Degradation is...

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

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Molecular Degradation Mechanisms

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



Molecular Weight Changes Permanently Through Chemical Reactions

Molecular Weight

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73

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

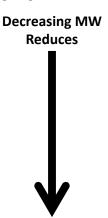
Molecular Weight

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Molecular Degradation Mechanisms

Tensile Strength
Elongation at Break
Impact Resistance
Fatigue Resistance
Creep Resistance
Hardness
Abrasion Resistance
Softening Temperature
Chemical Resistance



Molecular Weight

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75

Molecular Degradation



Molecular 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

Molecular Weight

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Thermal Oxidation

Resin Drying

• Storage ROO' + RH ROOH + R

Service

Molecular Weight Changes Permanently Through Chemical Reactions

2ROOH --- RO' + ROO' + H₂O

Molecular Weight

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77

Molecular Degradation



Chain Scission

- Compounding
- Molding

$$R - R \xrightarrow{Heat} R1 + R2$$

Molecular Weight Changes Permanently Through Chemical Reactions

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Hydrolysis

- Compounding
- Molding
- Storage
- Service

Molecular Weight Changes Permanently Through Chemical Reactions

Molecular Weight

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79

Molecular Degradation



UV Degradation

Service

Molecular Weight Changes Permanently Through Chemical Reactions

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Effects of Molecular Degradation

- 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 Weight

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81



COMPLEMENTARY TESTS



There are tests that provide clues that a plastic material may have undergone *molecular degradation*.

These results suggest molecular weight testing.

83

Complementary Tests



Visual

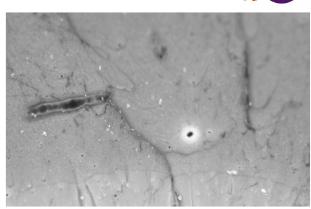
 Included black specs in part of on fracture surface





Visual

 Included black specs in part of on fracture surface



85

Complementary Tests



Visual

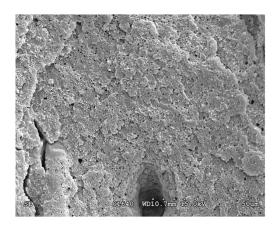
 Mud-cracked appearance on the surface





SEM

- Coarse fracture surface morphology
- Brittle fracture
- Micro-porosity



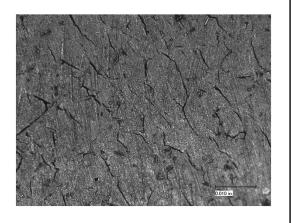
87

Complementary Tests



SEM

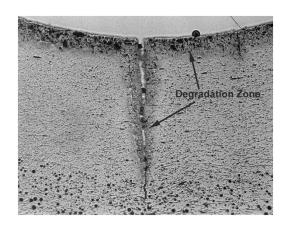
 Microscopic surface cracking





Cross-section

- Coarse Texture
- Darkened Color



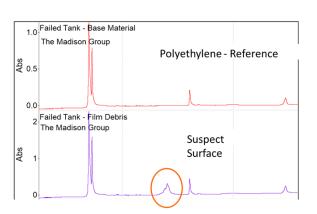
89

Complementary Tests



FTIR

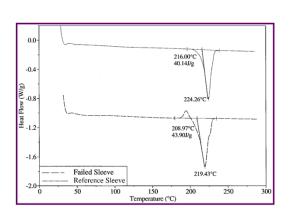
- Analysis of suspect surface material indicative of oxidized polyolefin
- Spectral bands ranging 1750 cm-1 to 1710 cm-1 broad





DSC

 Reduction in melting point or glass transition temperature



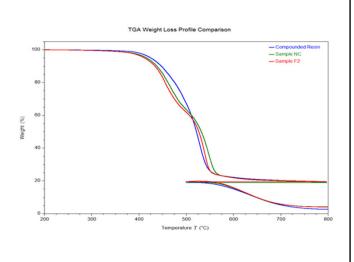
91

Complementary Tests



TGA

 Variation in weight loss temperature profile



Plastic Properties



Remember:

The properties of a plastic material are the direct result of the *Polymer Structure* and *Plastic Composition*

Molecular Weight

The Madison Group 608-231-1907

93

