

# Term Paper Introduction

## General Notes

- (i) Decide Vertical vs. Horizontal Approach
- (ii) Published, Peer reviewed articles are expectation
- (iii) No date limit on citations but you must read it & a review article, or book chapters books not strict published but they should not dominate
- (i) Do not cite web addresses as references
- (ii) Try to avoid writing a review article based on summarizing a review article, or book chapters
- (iii) Any more than 50 consecutive word match violates copyright law

## Possible Term Paper Subjects

- (i) **Vitrimers**: A chemical group that can be broken apart under certain conditions, while having thermoset characteristics at room temp. Can be considered a dynamic bond
- (ii) **Green Flame Retardants**: Traditionally Highly Toxic or produce toxic chemicals when heated. Cancer Causing usually. This focuses on developing one that isn't as toxic.
- (iii) **Bio-crystals**: Making mm x nm crystals with no defects. This small size warranted this time.  
**Example:** Carbon Nanotubes  
Needle like crystals which can be prepared from cellulose, hemicellulose, or others
- (iv) **MXene**: 'Maxenes'. Layers can be separated. Such as graphite being separated into individual layers of graphene. **Incredible Aspect Ratio**
- (v) **Glass Transition Temperature**: Super easy to measure. Popular topic of polymer studies but not really known. Nobel Prize worthy.  
How can we predict glass transition temperature without any assumptions?
- (vi) **Collection of Rare Metals**: Natural Oil Reserves running out. Flaking helps this, but horrible to environment.  
↳ Contaminates with excess natural disasters. Metals much harder to replace. Using by-products and will exhaust before oil. Found in low concentrations in seawater.
- (vii) **Porous Materials**: Used to assist in topic of (vi). Analogous used on space shuttles. Very brittle/fragile but remarkably flame resistant. Carbonaceous porous  
Can create non-metal catalysts with porous nts!
- (viii) **Extreme Temperature Polymers**  
↳ Being Scramjet can fly in very thin air at fast speed. Falcon HTV-2 also incredibly hot, compared to current record of cmauth 3. Used for weapons, but can turn into passenger travel, reduces trips to other continents to months of hours.  
Polymers need to be developed to survive 750-1000°C. Breaks temps but is less sensitive to a slow, safe, stable travel.
- (ix) **Non-metallocene Catalyst**: Carbon's surface has defects  $\rightarrow$  acts as catalytic centers. Can add other atoms to defects  $\rightarrow$  more active.
- (x) **H-bonding (Supramolecular synthesis)**: Technique to let monomers contact in non-covalent manner and lets you selectively design polymerization (usually random). Catalyst allows polymers to obtain in a desired way  $\rightarrow$  crystalline properties. Can also through H-bonding control this you can apply desired polymerization

**Pages:** 1 page to 10,000 pages. 1 page is harder to write. Subject chosen, date due, length.

**Review Draft:** Acts as a check point along with other milestones outlined in syllabus

ASK Questions!

Ishida knows his shit, don't plagiarize or copy references word-for-word!

# **Chapter 1**

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**Goal: Refresh information from ENGR145**

# Concepts and Nomenclature

Polymer = poly + mer 3 Repetition Units Oligomer = oligo + mer  
 ↑ multi + unit requires 2-4 units to be counted as poly mer  
 Sub Category a few + unit

Plus ics ← πλαστικός (Greek for plastic)  
 means to 'mold into'

Macromolecules: Contain both polymeric and non-polymeric large molecules

How many units to be polymers?

Rubber (AKA elastomers): polymers that deform elastically and to very large strains  
 ↳ become glass at low temperatures → become brittle (glass transition temperature)

Not repeating

00 "

0△0 "

0△△0 Beginning of structure

## Structure of Polymer Chains



## Copolymers

- **AAAAAA** Mono polymer
- **AAAAABBB** A,B-block polymer
- **AAAAA BBB** graft polymers
- **ABA BABA** alternating copolymer
- **A BBBA BA** random copolymer

Given Properties of homopolymers • Can you predict  
 A and B • Copolymer properties?  
 properties of A on one side, B on other like soap

even "mix" of properties: AB can be considered a monomer  
 unbalanced mix of properties: true random mixture  
 ↳ can be determined roughly with % of each

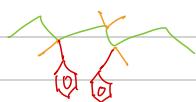
## Conformation vs. Configuration

Conformation: Structural change caused by chain rotation. Can be changed easily (reversibly) by changing temp.

trans: 'zig-zag' chain on a plane gauche: chain rotates  $\pm 60^\circ$  or  $-60^\circ$

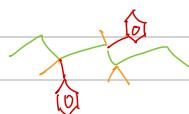
Configuration: Permanent structural difference caused during synthesis. Mild temp change does not affect this

a) Head-to-Head



Less likely to occur  
as this is energetically demanding

b) Head-to-Tail



Much less steric  
hindrance → thermodynamically more stable

## Stereoregularity (stereo isomers)

Isotactic

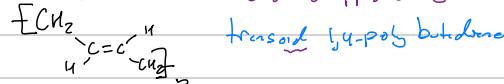
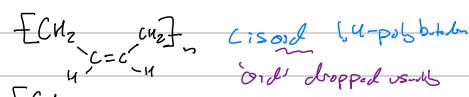
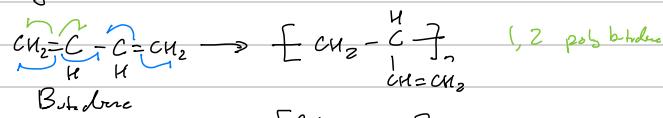
Can crystallize  
↳ Material looks shiny

amorphous

A tactic (Regular/Not polymers)  
↳ Doesn't crystallize → looks very glasslike

Most cost effective

## Regiosomers



## IUPAC Naming

- Add 'poly' to start of monomer name
- Not accurate! Polybenzoxazide is not wrong!

## Molecular Weight

Provide MW in Paper

Tensile Strength  
Cut 1 =  $10^8$  MW  
In half, more  
 weaker  
 $1/200$  strength

$$\text{Number Avg MW: } M_n = \frac{\sum N_x M_x}{\sum N_x} \quad \text{Related to tensile strength}$$

Basic average idea

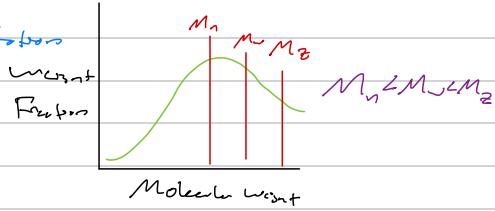
$$\text{Weight Avg MW: } M_w = \frac{\sum W_x M_x}{\sum W_x} \quad \text{How, } W_x = N_x M_x \rightarrow M_w = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

Average from weight perspective

$$\text{Z-average MW: } M_z = \frac{\sum N_x M_x^3}{\sum N_x M_x^2} \quad \text{Related to precipitators}$$

$$\text{Poly Dispersal Index (PDI): } PDI = \frac{M_w}{M_n}$$

$\hookrightarrow$  Higher PDI  $\rightarrow$  broader MW



# Molecular Weight & Macromolecules

## Various MW Measurement Methods

Method	Type	M.W. type	MW range
Colligative properties		Mn	
Boiling point elevation	Absolute	Mn	< $10^4$
Freezing point depression	Absolute	Mn	< $10^4$
Vapor pressure lowering	Absolute	Mn	< $10^4$
Osmotic pressure	Absolute	Mn	$2 \times 10^4 - 10^6$
Terminal group concentration	Absolute	Mn	< $10^4$
Light scattering	Absolute	Mw	$10^4 - 10^8$
Sedimentation	Absolute	Mw, Mz	$10^2 - 5 \times 10^6$
Intrinsic viscosity	Relative	Mv	$10^3 - 10^8$
Size exclusion chromatography(SEC)	Relative	Mn, Mw, Mz	$10^2 - 10^7$

Notes accurate but most convenient

With be discussed  
with Macromolecules

## Colligative Properties

- Add NaCl to water to lower Freezing Point
- Properties related to numbers

## Staudinger's finger

Hypothesis: stronger propylene molecule consists of aggregates of molecules  $\rightarrow$  size of aggregates should change as electronic structure of molecules is altered

## Approach: Hydrogenation of regular Benzene into a polycyclic aromatic hydrocarbon

Saturated cyclohexenyl ring

Materials Used: Polystyrene small oligomers of polystyrene

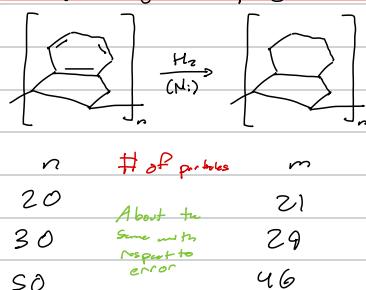
## Meas Method: Colligative property Measurement



Dilute Degree Polymerization as the product was aggregate of molecules

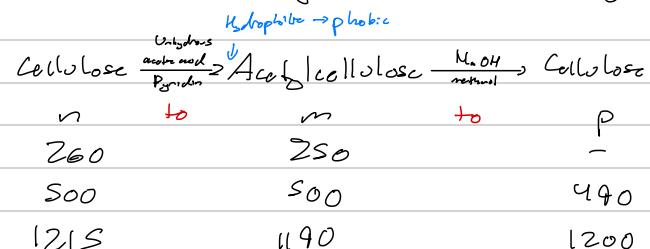
## Staudinger's Experiments

### Initial: Colligative Property Measurement



He was criticized for using small molecules

### Final: Acetylation and regeneration of cellulose; viscosity measurement



Directly from his paper, so mass viscometry measurement error

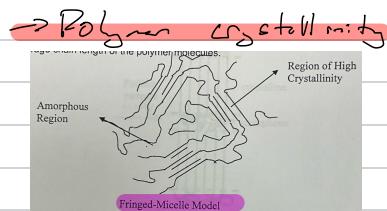
Critics stuck as they rebutted all they were arguing  
Covalent Bonds provided structure constancy

(like very cheap arm to make 'potent' laser)

Viscosity is more sensitive to larger MW molecules than smaller ones

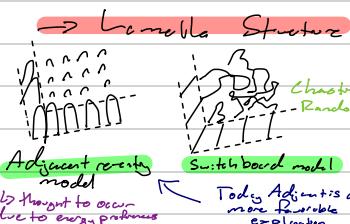
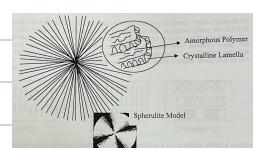
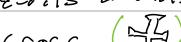
## Morphology

Def: Study of forms of polymer chains, such as crystal structure

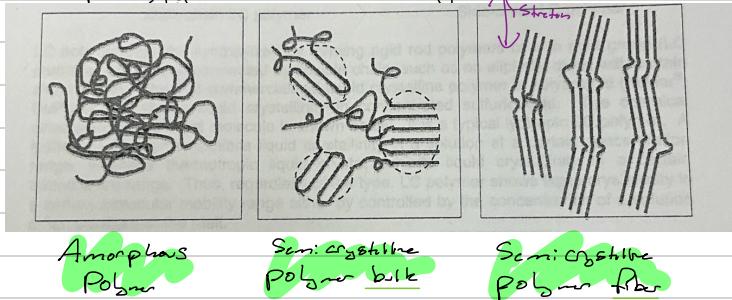


## $\rightarrow$ Spherulites

Polarized light reveals a molten cross



## Morphology Controls Stretching

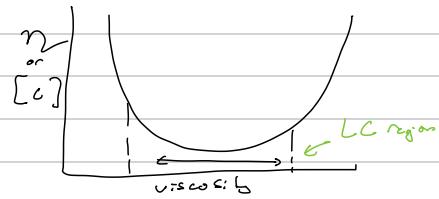


## Stretching

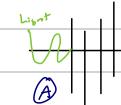
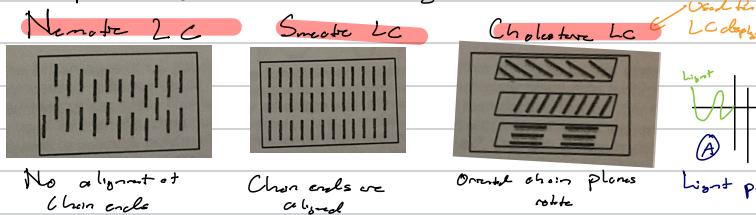
- Molecules realign along stretching direction.
- $\uparrow$  stretching  $\rightarrow$   $\downarrow$  intermolecular distance
  - ↳ leads to crystalline region formation
- Cracks are also observed along stretching direction
  - ↳ Thus the fibers or structural films are stronger along stretching directions

# Liquid Crystalline (LC) Polymers

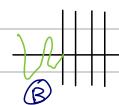
liquid = amorphous  
crystal = perfectly ordered } Two opposing words used to express unusual material  
that is neither completely amorphous nor ordered



## Types of LC Polymers



vs.



Sustaining orientation  
the layers so lighter  
rotate up and out

Allows microwaveable  
supplware

only dissolving  
conc. sulfone acid

**Thermotropic LC:** formed between certain temperature range  
**Liquid-crystalline LC:** formed between certain concentration range

ex: Aromatic Polyester

ex: Poly(p-phenylene phthalimide), polyaramid Kevlar



Main-chain  
type LC



Side-chain  
type LC

□: LC chromo phase

## Advantages

- (i) Lower viscosity in LC state than random melt/solvent
- (ii) Molecular alignment even in liquid state  $\rightarrow$  strong fibers

even bullet proof

## **Chapter 2**

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**Goal: Learn what and when to apply certain analytical techniques**

# Chromatography

You should always start by determining if it's a mixture or pure substance

"If you come into other substances; purify, purify, purify, and most importantly purify" - which

(i) Bring to high purity, then crystallize

(ii) If the material cannot be crystallized you must find a better way to purify

## Chromatography

(i) HPLC (High Perf. Liquid Chrom) ↓ (eluent) machines, change type  
↓ based on column and mixture used!

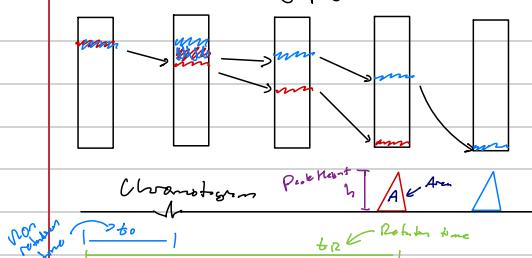
(ii) SEC (Size-Exclusion Chrom)

Chromo = Color

Graphy = Technique

Thin Layer Chromatography (TLC) indicates if compound is a mixture when exposed to UV light

## Column Chromatography



Columns use packing material in a separation column.

HPLC: use silica gel

SEC: use cross linked poly styrene gel

thus a Mobile & Stationary Phase

## High Resolution Fractionation

Gel Filtration: used in Fract. mode using porous particles where small molecules can get trapped in pores to travel and large ones flow around them.

## Analyses

Collected Fractions examined by spectroscopic techniques to determine concentration of particles eluted. ex spectroscopic techniques: Refractive Index (RI)  
Ultra violet (UV)

(i) Refractive Index: Most Popular ass't is different for molecules with diff. structure  
↳ not as sensitive to absolute mixture results

(ii) Ultraviolet: Order of Magnitude more sensitive

↳ not all molecules can absorb/react to UV

Combining these techniques allows you to check if mixture is homogenous or a copolymer

Mobile Phase = liquid → mobile phase called "eluent"

↳ Stationary Phase is usually a solid or liquid

↙ (Derived from Liquid Chromatography)

## HPLC

• High Degree of separation

→ Refinement of packing material  
(3 to 10 μm)

• Reduction of Analysis Time

→ Delays of about by pump

Used in tons of industrial studies!

## Advantages

- High Capacity, enabling batch analysis
- Superior quantitative capability and reproducibility
- Moderate conditions (i.e. Sample vaporization unneeded)
- Generally High Sensitivity
- Low sample consumption

Cannot use on solids which don't dissolve or evaporate

## Gradient Systems

- Isoconcentric System: Constant Eluent composition
- Gradient System: Varying eluent composition
  - (i) HPGC - high pressure gradient
  - (ii) LPGB - low pressure gradient

Typical one used

## Reversed Phase Chromatography

- Stationary Phase: Low Polarity  
→ Octadecyl group-bonded silica gel (ODS)
- Mobile Phase: High Polarity  
→ Water, methanol, acetone, etc & salt solutions

Hydrophobic → Hydrophobic surface charge

en: Phenols are hydrophobic

so it avoids hydrophobic surfaces.

Untreated silica gel is usually used (Acidic)

Acid/Base interactions > H-bonding ones

Detectors: UV-VIS Detectors, Refractive Index detector, electrochemical detector, mass spectrometer, etc

## Sizing Exclusion Chromatography

- Molecules separated based on size (based on bulkiness)
- Usually applied to large macromolecules
- Does not care about hydrophobic/hydrophilic

Think of it like trying to explore a tight cage

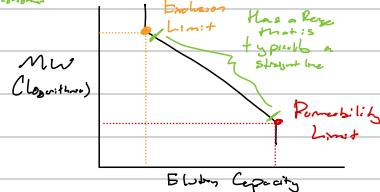
- Huge molecules come out first as small ones need to go through a lot of pores
- Uses cross-linked polystyrene → Created with vinyl aromatic monomers
  - ↳ This means most polymers will interact with the substrate

## Separation Principle

→ Molecules  $>$  Pore size cannot enter!

For molecules that can enter, there is a inverse logarithmic relationship

P.I. (or monodispersed PDA)  
UV (single/wavelength/multiple wavelengths), Fluorescence, Electrokinetic



You can determine  $M_n$ ,  $M_w$ ,  $M_z$  using Chromatographic techniques (with software)

# Infrared Spectroscopy

Photon in → Photon out

↳ Invisible radiation outside of the red

Used because it has exactly the right energy to see molecules moving at a certain frequency (which requires energy)  
 ↳ As long as molecular structure is different, IR will be different too!  
 Gives you group formations usually

Detects Vibrational Motion

## Uses of Vibrational Spec

- Recognition of functional groups
- Ident. of spectra of individual molecules
- Determination of molecular structure

## Advantages

- Sensitive, Rapid
- Spectra easy to see

## Disadvantages

- Chemical process
- Hard to interpret.

## Spectral Analysis

A spectrum completely defined when following spectral parameters are specified

- The frequencies
- # of constituent bands
- Band shapes
- Band widths
- Amplitudes or intensities

Peak Height is usually called intensity, but  
 you should really use integrated intensity

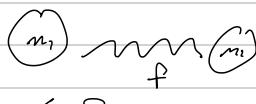
## Model For Vibrational Spectroscopy

↳ Point masses bonded with a Hookean Spring

Allows us to see bonding, stretching, bending, wagging, etc.



$Z_n - 6$  is number of bands,  $n$  is # of atoms/molecules



Hookean spring  
resting force:  $f$

← Displacement →  
(z)

From 2nd order DE  $m_1 r^2 = \frac{m_1 m_2}{m_1 + m_2}$   $\mu$  constant

$V = \frac{1}{2\pi c} \left[ \frac{f}{m_1} \right]^{1/2}$

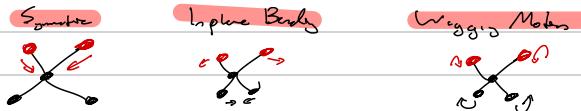
Frequency



- Double Bonds
- Have much higher Frequencies than single bonds.

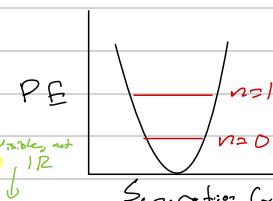
• Frequency Higher with smaller masses!

## Analysis of Methylene Models



$$E_v = (n + \frac{1}{2}) \left( \frac{\hbar}{2\pi c} \right) \left( \frac{f}{m_r} \right)^{1/2}, \text{ for integral values of } n \text{ (vibrational quantum number)}$$

$$\Delta E_{\text{fundamental}} = h\nu_0 = \text{Optical Frequency}$$



Only #1 is visible, can only see n=0 to n=1 and back

## Selective Rules for Vibrational Spectroscopy

### (i) Infrared

- Polar bonds are strong
- Dipole moments present
- Charges in permanent dipole moment upon vibration

- Charge is polarization of molecule
- Non-polar or homonuclear bonds strong in the Raman effect

### (ii) Raman

## Characteristic Group Frequencies

Use characteristic Frequency table to determine groups!

- Func groups have same frequencies regardless of nature of remaining molecule
- Observation of certain frequencies indicates which groups present
- With frequency not present, then func. group is not either

## Molecular 1D-Basis

- UV-vis spectrum is a 'fingerprint' of the molecule
- Data must be from pure compounds!

## CWIR Evolution

- Albert Michelson: Michelson & Morley → Nobel Prize

↳ Prof. of Physics at Cesc

- William W. Coblenz: Established IR spectroscopy as an analytical technique  
↳ Attended Cesc as an OG student

- Jack Koening: First Raman study of carbon

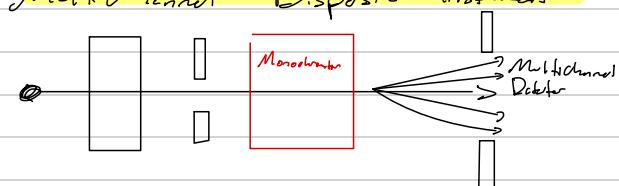
- H. Isidor: FT-IR analysis. Optical Techniques

## Dispersive Infrared Instrument



Solution

## Multichannel Dispersive Instrument

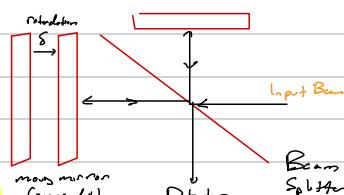


## Disadvantages

- Slow Scanning Process
- Limited energy throughput  
↳ Dispersion loses energy
- Digitalizing difficult

## Michelson Interferometer

So, energy lost!



## Fourier Transform (FTIR) Spectrometer

- Encodes the info in an interferogram using Michelson interferometer
- Performing Inverse Fourier Transform to change Distance → Frequency  
↳ FFT used to transform Interferogram to Spectrum
- Computation:  $I(x) = \int_{-\infty}^{\infty} B(u) e^{2\pi i ux} du$   
 $B(u) = \int_{-\infty}^{\infty} I(x) e^{-2\pi i ux} dx$

## Advantages

- Jacquinot: Energy Throughput ↑
- Fellgett: Multiplex
- Connes: Frequency Accuracy

FTIR Originally Studied by Frank Sombret

No Disadvantages  
to using FTIR

# Nuclear Magnetic Resonance Spectroscopy

## Nuclear Magnetic Resonance (NMR) Spectroscopy

- Obtains spectra from unique magnetic structures of the nuclei
- Details nuclei Magnetic Property

- (i) Liquid
- (ii) Solid State
- (iii) MRI Imaging

3 types, but same principle. Diff conditions

### Advantages

- Highly Specific
- Simple Interpretation

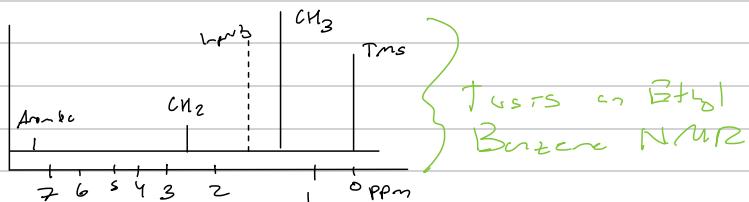
### Disadvantages

- Low Sensitivity
- Measurement time Long
- Difficult to work with complex mixtures
- Very Expensive to operate & maintain
- Solubility limitations of polymers

500-600+ MHz preferred  
1.1 GHz on campus!

## How does NMR Work?

- Some atomic nuclei behave as tiny bar magnets when placed in field  $\rightarrow$  alignment
- $\hookrightarrow$  They magnetize about the magnet at its Larmor frequency
- Hit Nuclei with pulse to knock its spin, so it will flip spin up back to original state
- ppm reported usually
- Software used for reporting, cause inverse FT to go from func of time to frequency  
 $\hookrightarrow$  By Def, NMR is Fourier transform, so it's not called FT-NMR
- Present molecules show - $\nu$  vs one spot or. You can see impurities as well
- Farthest left are most  $\nu$  (ppm), meaning they furthest from Larm Frq.
- TMS is  $\text{Si}(\text{CH}_3)_4$  and is one of the most positive compounds you can find, used as baseline
- NMR has a superconductor magnet - needs to be very cold



## NMR Signal to Noise Ratio

$$\frac{S}{N} = \gamma N I (I+1) \left[ \frac{B_0}{T} \right]^{3/2} F \left( \frac{\Omega V_0}{b} \right)^{1/2}$$

- $\Rightarrow \gamma$  is magnetogyric ratio of nucleus
- $\Rightarrow B_0$  is external magnetic field
- $\Rightarrow N$  is # of magnetically active nuclei
- $\Rightarrow T$  is sample temp

- $\Rightarrow Q$  is quality factor of resonant circuit
- $\Rightarrow F$  is filter factor
- $\Rightarrow b$  is bandwidth of detector
- $\Rightarrow V_0$  is volume of sample

## General Notes on NMR

- Increased chemical sensitivity w/ applied magnetic field  
 $\hookrightarrow$  Can study more neighbors w/ lower frequency
- NMR Spectrum revealed that polyethylene can be short-chain branched  
 $\hookrightarrow$  Butyl and ethyl groups are most frequent
- Intensity Ratio comes from Pascal's triangle with # nub.. neighboring interactions

### Iso tactic Peaks

### Syndiotactic Peaks

### A tactic Peaks



# Thermal Property Analysis (DSC & TGA)

## DSC (Differential Scanning Calorimetry)

- Measures the flux of heat
  - ↳ Temperatures & heat flows associated with transitions in materials
- Calorimeter: Measures heat into and out of a sample
- Differential Calorimeter: Measures heat of a sample relative to a reference
- A DSC does both of the above and heat sample w/ linear temp. ramp

Endotherm: Heat flows into system  
Exotherm: Heat flows out of system

- Crystalline Compounds have a melting endotherm
- Makes Instrumentation consists of usually 4 parts

↳ Usually Use Aluminum unless sample is reactive w/ Al  
•  $T_g$  readings are about 100x weaker than the other technique commonly used today

Exotherm Events: Crystallization, Solid-state Transitions

- Lack of Peak Thermograms are 2<sup>nd</sup> order transitions & Thermograms

↳ With peaks, these are 1<sup>st</sup> order transitions

- Glass Transitions (second-order transition)

→ 2<sup>nd</sup> order transition

→ characterized by change in heat capacity

→ appears as a step with the midpoint being the reported  $T_g$

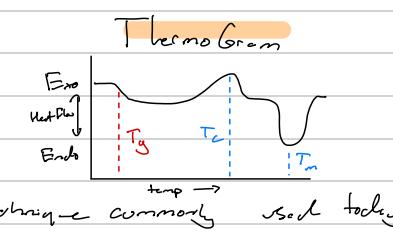
→ Small Endo peak may appear due to shippers / purity issues

- Enthalpy of Fusion given as area under melting curve

- Fundamentals based on Unit Heat Equations

$$T_m = T_o - \frac{RT_o^2 \chi}{\partial H_o} \cdot \frac{1}{f}$$

Look for  
Thermograms  
in research



Enthalpy relaxation  
phenomenon



## Reversing and Non-Reversing Contributions to Total DSC Heat Flow

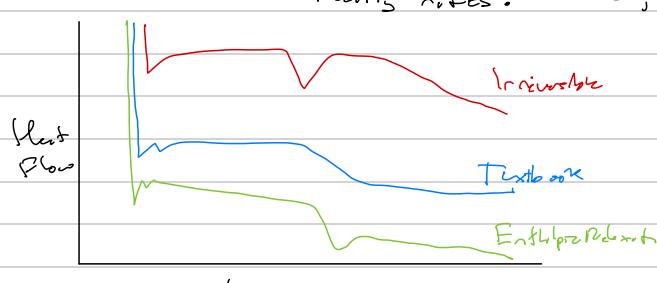
$$\text{Total Heat Flow} \rightarrow \frac{dQ}{dt} = C_p \cdot \frac{dT}{dt} + f(t, T)$$

Non-reversible heat component  
Reversible signal

- Time domain to Frequency domain, but DSC doesn't contain an integrator

Temperature Modulated DSC: Determines heat capacity and separates heat flow into reversible and non-reversible events

↳ Heating rates: 0-8 °C, Period: 60sec, Amplitude, +/- 1 °C

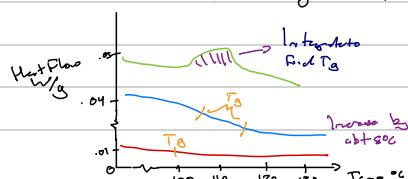


## Reversible vs. Non-Reversible Transitions

Reversible: Glass Transition, melting

Non-Reversible: Crystallization, Oxidation/Reduction, evaporation, curing

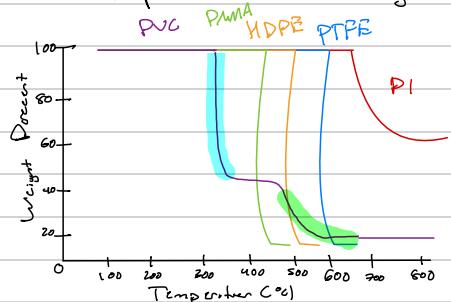
## TMDSC Thermograms for Nanocomposites with 50 wt% of Polystyrene



## TGA (Thermogravimetric Analysis)

- Excellent for studying thermal degradation of polymers
- Use a balance and measure weight as a function of heating
- **Differential Thermal Analysis (DTA):** Old technique which measured temp. difference  $\Delta T = T_s - T_d$ , between a sample and reference material. Not used as much/still today.
- Measures the residual weight and rate of weight change as a function of temp or time
- **TGA Measures:** Thermal Stability, Composition, Decomposition Kinetics, Moisture & volatile content, estimated T<sub>d</sub> to me. Cannot probe chemical structure  
 ↳ Allows you to study fragment structure when combined with structural analysis techniques

### Example TGA Thermograms

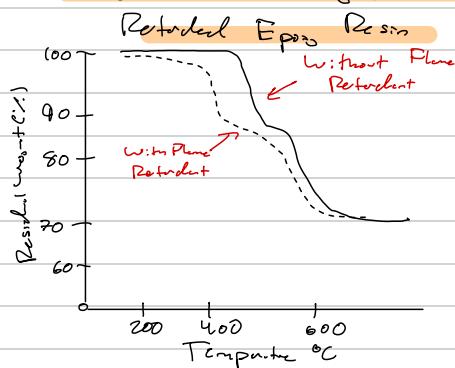


### What's going on with PVC?

• PVC is so complex w/ HCl and wants to lose -Rst  
 -Rst → drop-off

Forms carbon radicals  
 upon degradation →  
 creates C=C bonds  
 leads to coloration change.  
 Main chain degradation is del. drop!

### Thermo-oxidative stability of a Flame Retardant Epoxy Resin



### • Doublet Components

- Allows different polymers to be compared on the same grounds

↳ Flynn-Wall & Ozawa Isoconversional Method of Determining Activation Energy of Degradation

→ Can plot inverse temperature ( $1/T$ ) using isoconversional data, which can be plotted against  $\ln[\text{Rate}_0/\text{Rate}]$  to get a straight line whose slope is the activation energy

### • Temperature Modulated Thermo-gravimetric Analysis (MTGA)

↳ Perform Inverse Fourier Transform on Derivative Plot to get E<sub>a</sub>

→ This Technique allows you to analyze the frequency of the activation energy changes  
 ↳ Gives an Activation Energy Spectrum!

### Activation Energy

Good Journals don't

Accept single analytical result

### TGA-based hyphenated techniques

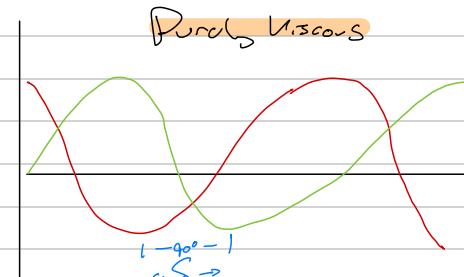
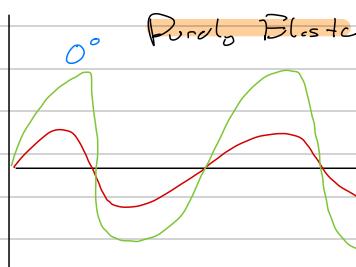
- TGA measures weight quantitatively
- TGA allows controlled decomposition
- Evolved gases are difficult to separate
- Reactor analysis of evolved gas minimizes secondary structure formation
- **DSC-TGA:** Measures both heat flow & weight changes as a function of temp or time  
 ↳ Simultaneous DSC-TGA  
 ↳ Separates temperature. Distinguishes b/w endo/exo transition events that look weight change from those that do involve weight loss & degradation

melt & crystallization

# Dynamic Mechanical Analysis

## Dynamic Mechanical Analysis (DMA)

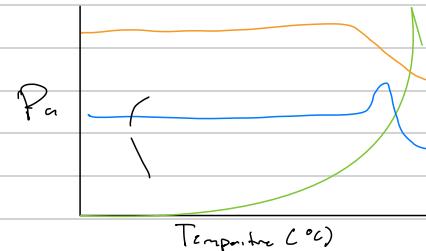
- Sample moves in sinusoidal motion instead of static/stress techniques
  - ↳ Bottom line: static stress actually changes the polymer structure
- Sinusoidal stress on a sample applied to measure stress in terms of phase lag
- You can learn:
  - (i)  $G'$ : storage modulus (recoverable energy)
  - $G''$  peak is  $T_g \rightarrow$  (ii)  $G''$ : loss modulus (irrecoverable energy lost as heat)
  - (iii)  $\delta$  or  $\tan \delta$  (degree of viscoelasticity)
  - (iv)  $T_g$  & Zards of modulus are sensitive than DSC
  - (v) Gelation & Tvisc is associated with Thermoset Polymers mostly
- $\tan \delta = \frac{G''}{G'}$  regardless of sample size
- Pure elastic samples have no  $\delta$  (0°) true delay  $\rightarrow$  phase angle  $\delta = 0^\circ$
- Purely viscous samples have a phase angle  $\delta = 90^\circ$



$\delta$  vs.  $\tan \delta$ :  $\tan 90^\circ$  is undefined so  $\tan \delta$  is used if  $\delta$  is small. Used for large measurements.

### Polymer DMA Spectra

- (i)  $G'$  is orange
- (ii)  $G''$  is blue
- (iii)  $\tan \delta$  is green
- (iv)  $T_g$  found at top of  $G''$  peak or  $\tan \delta$



Difficulty obtaining  $\tan \delta$  of  $G'' \rightarrow$  use  $\tan \delta$   
 $T_g$ . Otherwise  $G''$  peak is more rigorous to report

- DMA spectrum compares thermosets these polymers have no  $T_m$
- Rubbery plateau is longer for larger MW values
- Gelation of Polymer Solutes
  - ↳ Increase temp of liquid monomer  $\rightarrow$  starts to polymerize and viscosity ↑
  - ↳ At some point, liquid sample  $\rightarrow$  more solid like (gel)
- Polymer undergoes 2 transitions
  - ↳ Gelation, and Viscoelastic
- Beyond Gelation temp, you cannot process material

Use non-Fourier based analysis for more rigorous study  
 ↓  
 Gelation Occurs when  $G'$  and  $G''$  cross (not fully accross but used for convenience)

# Chapter 3

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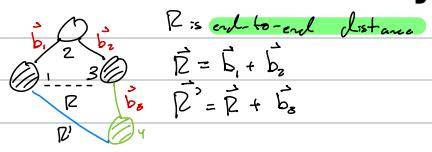


## Goal: Polymer Physics

*Plenty of equations will be discussed but not needed to memorize complex ones, included for explanation*

*↑ Simple equations are always better!!*

# Introduction to Polymer Physics



$R$  is end-to-end distance

$$\vec{R} = \vec{b}_1 + \vec{b}_2$$

$$\vec{R}' = \vec{R} + \vec{b}_3$$

## **Chapter 5**

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**Goal: Study polymer & composite processing techniques**

# Composites & Nanomaterials

## Composite

- Fiber used to reinforce an otherwise weak polymer/material
- Fiber and Matrix combined to create a strong material with certain desired products
- Define: A heterogeneous material consisting of two or more materials

↳ If upon mixing you yield a homogeneous substance, it is no longer a composite

- Exhibit properties of its component materials

↳ one component would consist of more rigid/butter/stronger properties

- New properties that do not exist in individual component will often appear - Synergism

- Human body made up of composites: tendons, teeth, bones

- Classifications of Composites

(i) **Engineering composites**: Fibers or fillers with millimeter & micrometer size used as reinforcement

↳ Poor fiber/matrix interface can initiate cracks

(ii) **Microcomposites**: At least 1 of the components has nanometer dimensions

↳ Small amount of reinforcement exhibits significant prop. improvement

(iii) **Molecular composites**: Rigid Rod molecules are used as reinforcement

## Other Jargon

→ Reinforced Polymers - Composites w/ Fibrous materials

→ Filled polymers - polymers w/ particulate fillers

→ High Performance Composites -  $T_g > 200^\circ\text{C}$  e.g. carbon fiber reinforced polyimide

→ Low Performance Composites - e.g. injection molding of filled PE

→ Fibers - Reinforcing strength of weak polymers properties tend to be anisotropic

→ Filament - Diameter typically between several micrometers to several tens of micrometers

→ Extruder - A filler w/ almost no reinforcement effect used to reduce amount of plastic required

→ Fillers - Materials other than continuous fibers

→ Strand - A few hundred to few thousand filaments are bundled together by a film former

→ Roving - Many sets of strands are bundled together

## Which ones are composites?

yellow = yes; blue = sometimes

- A. Consolidated two miscible polymers X muscible, so no heterogeneity
- B. Consolidated mixture of calcium carbonate powder and polypropylene Consolidated Mixture!
- C. Sugar/water mixture X Sugar dissolves water → no heterogeneity
- D. Cotton fiber consolidated by phenolic resin materials heterogeneous & consolidated
- E. Phase-separated diblock copolymer X it depends on choice of comonomers
- F. Tire made of carbon black and polybutadiene First industrial nanocomposite
- G. Bullet proof jacket made of liquid crystal molecule, Kevlar X Only one material, Kevlar units own interparticle
- H. Consolidated two immiscible polymers X it depends on the properties of individual polymers
- I. Mica and PE powder mixture

**Caution:** Polymer Blends are consolidated immiscible polymers but not composites depends on A & B properties

## Raw Materials for Composite Manufacturing: Reinforcements & Fibers

### (i) Fibers

Inorganic: Glass fibers, Carbon fiber, alumina fiber, silicon fiber  
 good wear resistance → Organic: Polycarbonate fiber, PE fiber, polybenzoxazole fiber Dosed with butter

### (ii) Fibers ← Reinforcement to be bonded

Ordinary portlandite fibers: Silica, wollastonite, calcium carbonate

Whiskers: SiC, carbon made of single crystal (no molecular/atomic defects)

Nano fibers: C<sub>60</sub>, carbon nanotube, graphene, MXENE

Functional Nano fibers: Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Quantum dots (CdS, CdSe, InAs)

white paint → gives specific color based on size of metals

Raw Materials for Composite Manufacturing: Matrix Used to transfer stress between Fibers or Fibers

### (i) Thermosetting Resins

Unsat. PB, vinyl ester, epoxy, polyester, polycarbonate bisimide, cyanate ester, polymers, polyesters.

### (ii) Thermo plastic Resins

a) Ordinary Thermoplastics: Nylon, polycarbonate, polybutylene, PP,

b) High Performance Thermoplastics: Poly sulfone, polyetherimide, polyimide

Composites IPI: Tennis Rackets, Bridges, Bicycles, Golf Club Head, SKis, Some Floors, Atoms Spine Sutures

Diamond is a pure carbon material but can be burned (long carbon w/o protective coating) → March 22 max to date

→ Hypersonic Jets: Boeing X-51A Scramjet, Russian hypersonic missile, may soon hypersonic missile (March 5 - March 7+)

→ Need a light material that survives 750-1000°C? no such material exists right now

→ Developing a Commercial Hypersonic Jet must not produce a deafening sonic boom

Impact Strength  
tensile strength inversely proportional

## Typical Measured & Tested Property Measurements

Mechanical: Tensile Strength, Coefficient of Thermal Expansion, Dynamic mechanical analysis (DMA)

Tensile  
Compression

Thermal Coefficient of  
Thermal Expansion

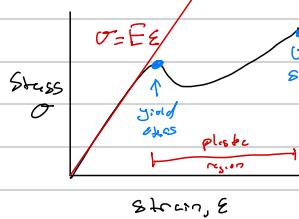
HDT → Heat Distortion Temp

Thermomechanical

If composite material CTE differs → breaks from shearing

## Universal Testing Device & Location

Uniaxial tensile test



Arcu curve

E = Modulus of Elasticity = Young's Modulus

Some use 3 point bending test

→ Hardly useful in accurate piping but used a lot for industrial applications

→ This is bc some materials don't like being pulled

→ Chug Impact Tester used as well

Adding Calcium  
Carbonto to PE  
causes tensile strength  
to decrease.

## Addition of Fillers

### Example: Billiard Balls

- Billiard balls need certain properties to move as desired ← Incident & reflective angle should be as planned
  - ↳ The ball needs a certain designed density
- To increase density, add a filler that greatly decreases the mechanical properties of a polymer
- Fillers into polymers reduce composite cost as filler cost < polymer cost

## Specific Modulus / Specific Tensile Strength of Composites ( $\frac{E_{\text{pu}}}{\text{density}}$ ) $E \frac{\text{GPa}}{\text{cm}^3}$

- Materials appear to be strong but look in specific tensile strengths & modulus

There is no carbon fiber that is good in both strength & modulus

• Carbon (P120): ↓ Strength, ↑ Modulus

• Carbon (T1000): ↑ Strength, ↓ Modulus

• Plot: Strength vs. Modulus

## Advantages of Composite Materials

- (i) Reinforcement of the resin  $\rightarrow$  increased tensile, flexural, compression, impact strength, and rigidity
- (ii) Increased size stability
- (iii) Increased fire retardancy
- (iv) Corrosion protection
- (v) Improved electrical properties
- (vi) Coloring
- (vii) Improved Processability: good mixing controlled viscosity, controlled orientation of fibers

## Prediction of Composite Mechanical Properties

- If reinforcing fiber fbs at smaller than the matrix longitudinal strength is:

$$\sigma_{in} = \sigma_{fu} V_f + \sigma_m V_m \quad (1)$$

$\sigma_{fu}$ : fiber tensile strength  $\sigma_m$ : stress carried by the matrix  $V_f$ : fiber volume fraction

$V_f$ : fiber volume fraction  $V_m$ : matrix volume fraction

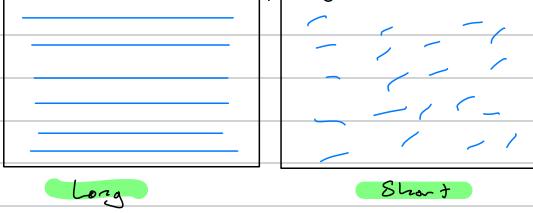
Short Fiber composite fail catastrophically - Fused for everyday use

- Different fibers/matrix should be used for different applications

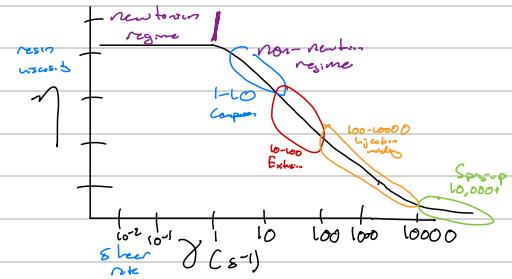
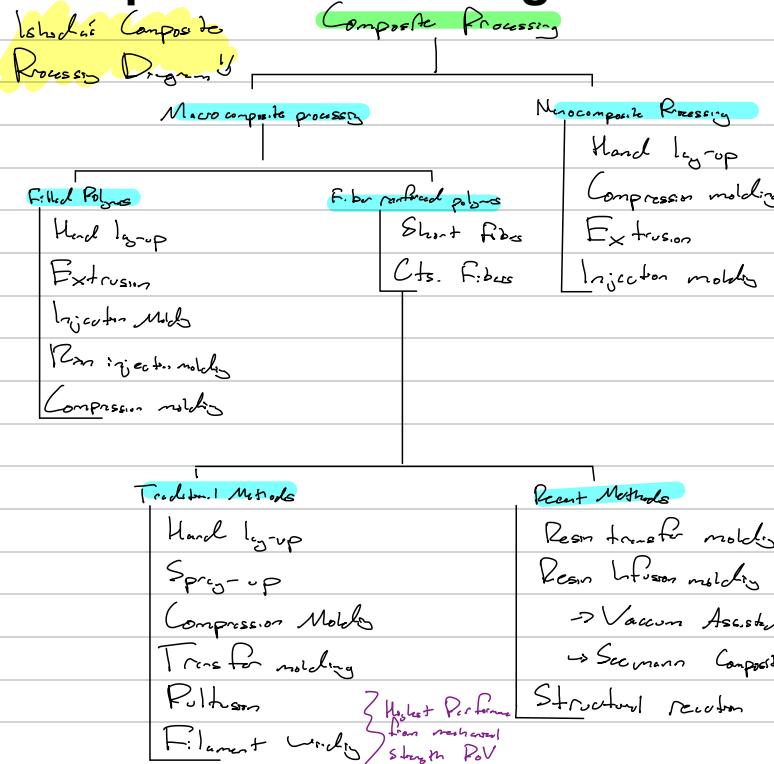
## Long vs. Short Fiber reinforcement

• Short Chopped fibers are less effective than long pts. fibers in reinforcing materials

- Cracks will only propagate if it exceeds its Griffith crack



# Composite Processing



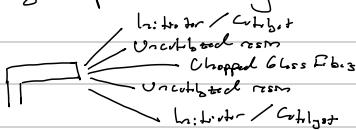
## Hand Lay-up Molding

- Most labor intensive
- Layer  $\rightarrow$  Resin  $\rightarrow$  Layer  $\rightarrow \dots \rightarrow$  Squeeze out bubbles  $\rightarrow$  repeat as desired "Lay-up"
- After Lay-up, cover with
- **Operations:** A reinforcement in a form of a cloth or mat is placed on a mold and liquid resin is placed on it

- Advantages:**
- i) Product design versatile
  - ii) Mold making is fast
  - iii) Low Capital investment

- Disadvantages:**
- i) Labor intensive
  - ii) High scrap rate
  - iii) Low productivity

## Spray-up Molding



**Note:** Catalyst is not forced to mix with resin  $\rightarrow$  material intensive

- **Operations:** Cuts fiber dropped up at the spray-up gun end fraction. Fibers are sprayed onto the mold surface along with the initiator

Do not depend on Spray-up products if your life is at stake

## Example: Fake rocks in amusement parks & gardens/zoo's

- Eff. Resin is much lower as grinds not mix resin with initiator
- **Room Temperature Curing**
  - Much cheaper than buying a large furnace
  - Time constraints are to issue
- **Advantages:**
  - i) Mold  $\rightarrow$  Small Particle Size
  - ii) Leads to ↑ up pressure
  - iii) 2-3 times improved productivity to hand lay-up
- **Disadvantages:**
  - i) Produces Strong Needs Fire Dept Approval  $\rightarrow$  a carcinogen
  - ii) Environmental Concerns  $\rightarrow$  Added expenses
  - iii) Still labor intensive
  - iv) Still high scrap rate
- Carbon fiber trapdoor failure of trap door is possible
- (v) Low productivity

## Compression Molding

- Composite material placed between two ends of mold
- High productivity but also high energy requirement due to high composite viscosity (Needs strong hydraulic press)
- If partial unfilled portion exists, then the product is scrap!
- If excess material is used you get an auto-welded portion in labor intensive removal/cut (Called teflash)
- Most versatile out of three techniques (not specialized) but still labor intensive
- **Operator:** A material is placed on a heated plate and squeeze the material with a powerful hydraulic unit using an open-mold approach

**Advantages:** (i) Good Productivity (general)      **Disadvantages:** (i) In-trim shaped objects cannot be molded

(ii) Mid-Rate Productivity (composites)

(iii) Not too labor intensive

(ii) Some labor is needed to clean the flash

(iii) Energy intensive

☒ (iv) Most versatile method Geometrically limited because of flash formation

↳ Due to need of very strong hydraulic press

## Transfer Molding

- Since Moldless Compression Molding → closed mold
- Material is not placed in mold cavity! ✓ it takes a lot of energy to push it through  
↳ Transfer into cavity by using hydraulic pressure
- Squeeze composite dough into mold through sprue → only need to cut sprue material

**Advantages:** (i) Low Labor

**Disadvantages:** (i) High Energy (Energy intensive)

(ii) Price Money → No Flash produced

## Resin Transfer Molding

- Transfer low viscosity resin and then make a porous product with chopped fibers → makes a pre-gel shape to put into mold to fill cavity with the resin
- Push Preform into mold cavity

**Example:** Making a boat

Polymerized after being filled toward

- Removes joint creation when processed → much stronger (radius stress conc.)
- Can use multiple injection ports from the same pump
- Porous density/tightness fibers is/are determined by desired type of product
- Resin is not ultra ultra viscous but is more viscous than honey for example

**Advantages:** (i) A large product can be molded in one shot

**Disadvantages:** (i) Resin not be low viscosity (less than 1 Pa·s @ op. temp)

(ii) Energy (Effort + low pressure)

(iii) In-trim shapes cannot be molded

## Vacuum Assisted Resin Transfer Molding (VARTM)

- Same process as resin transfer molding, but is finished by a vacuum  
↳ Can thus use higher viscosity resins
- No unique advantages / disadvantages to resin transfer molding just easier

## Injection Molding

- Usually used to make small intricate-shaped products
- Comes two techniques: (i) Extension and (ii) Plunger-type injection
- Screw rotates in a hot barrel  $\rightarrow$  Polymer drops onto砧木 (liquid)

**Properties**  $\hookrightarrow$  Screw is cut opposite to usual  $\rightarrow$  rotates clockwise to move the polymer forward

- Molten Polymer collected at head of screw, then the screw is used as a plunger once reservoir is large enough
- Most automated technique - e levers arms can be used for many operations

$\hookrightarrow$  Productivity is high and scrap rate is low (no flash) but machines are very costly!!

**Advantages:** (i) Can make very intricate objects

(ii) Low scrap rate

**Disadvantages:** (i) Expensive

(ii) High Production

(iii) Highly automated

(iv) Capital Intensive

## Reaction Injection Molding

- Instead of using already polymerized materials, it uses non-polymerized ones and polymerizes it then later in the machine
- Compound sent to impingement mixer head where compounds react quickly to polymerize
  - $\hookrightarrow$  Industrial compounds can be much lower viscosity which is good for ease of production and energy use
- Can make products in one shot with this as well

**Examples:** Jet skis, Bumpy Snowmobiles, Any place where water is always present (uses hydrophobic chemicals usually)

- Creates remarkably strong materials

**Advantages:** (i) Very rapid cycle time (<2min) **Disadvantages:** (i)  $\hookrightarrow$  U.S. polymers you can use!!

(ii) Low energy requirement

(ii) Limited number of polymers can be made

(iii) Chemicals can be air and/or water sensitive

## Resin Transfer High Performance Processing Technique

**Examples:** I-beams, Sound proofs, Airplane parts, Various Tubings  $\hookrightarrow$  Can also make telephone buss (sound barrier or molds)

- Can make any product that has a constant cross sectional area
- $\hookrightarrow$  High productivity and performance  $\leftarrow$  doesn't sound like a polymer when struck

$\hookrightarrow$  Fibers wet with liquid resin is pulled through a heated die where the resin gels and vibrates

**Advantages:** (i) Very high mechanical strength

**Disadvantages:**

(i) Only composites with constant cross-

sectional area can be made

$\hookrightarrow$  Not the for batch operation, only limited for continuous ones

(ii) The only truly cont. process for

cts. fiber reinforced polymer

$\hookrightarrow$  This is a High Performance Technique

## Filament Winding High Performance Processing Technique

- 'Mandrel' is the term used instead of 'mold'

- Mandrel rotates @ constant speed

- Egot feeds fibers under tension, moves back and forth across rotating Mandrel

- Fibers must be under equal tension to avoid breakdown fracture

$\hookrightarrow$  If fibers are all under the same constant tension, extremely strong composites can be made

$\hookrightarrow$  High fiber content under uniform tension are the key to developing high performance composite <sup>Highly</sup> <sup>Plastic</sup> <sup>Put</sup>

**Examples:** Massive Fuel Tank for Saturn rocket used for the upper stages, Pressure tanks, Golf Club shaft, Rotor blade

$\hookrightarrow$  Removes Mandrel from small openings <sup>like Rotor blade</sup> (i) Make mandrel out of plastic which dissolves under high pressure heat until

(ii) Dissolve <sup>like Rotor blade</sup> into the resin to remove the mandrel

**Advantages:** (i) Strongest composite of all **Disadvantages:** (i) Low productivity and expensive

$\hookrightarrow$  costs are very high and very time consuming

processes methods

(ii) Does not require constant cross-

sectional area

$\hookrightarrow$  This is a High Performance Technique

**Advantage:** (ii) of Filament winding still holds as this is a batch process, production does not continue

it will continue