

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 \leftarrow books not strictly prohibited but they should not dominate
- (iv) Any more than 50 consecutive word match violates copyright law

No-nos!

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) **Glass Plasma 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
 - Defects lead to reduced material strength by design
 - Biodegradable
 - 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. \hookrightarrow Contaminates with various 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. \checkmark Can create non-metal catalysts with porous materials!

Extreme Temperature Polymers

$\xrightarrow{\text{Moog}}$ Boing Scramjet can fly in very

thin air at fast speed. Falcon

$\xrightarrow{\text{Hoch}}$ HTV-2 also incredibly hot, compared to

current record of cmach 3. Used for

weapons, but can turn into passenger travel, reduces trips to other continents to months of hours.

Polymer needs 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 polymerizations (usually random)

Catalyst allows polymers to obtain in a desired way \rightarrow crystalline properties.

Can also through H-bonding and this

you can apply desired polymerization

Pages: 1 page to 10,000 pages. 1 page is harder to write. Subject Chosen, Definite 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!

Reflection - 10/30/24

- Journal names should be abbreviated
- More Quantitative data is better, less too heavily relied on qualitative observations
- Figures should be used to enhance your work — People are lazy and want something to catch their eye/attention
 - \hookrightarrow In the real world: Graphical abstracts are used to catch the attention of readers
- Do not cite web addresses only! May be obvious in text already, but today it's not acceptable
- People did not use consistent citation styles (most likely as they were generated by a non-credible source)
- Cosine factors and context are both important! Style should be consistent

Put this feedback, Pagan notes, and Grade onto the github repo!

(60, 79.4, 100)
 $\frac{\text{low}}{\text{avg}} \frac{\text{high}}$

Chapter 1



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 ← πλαστικού (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)

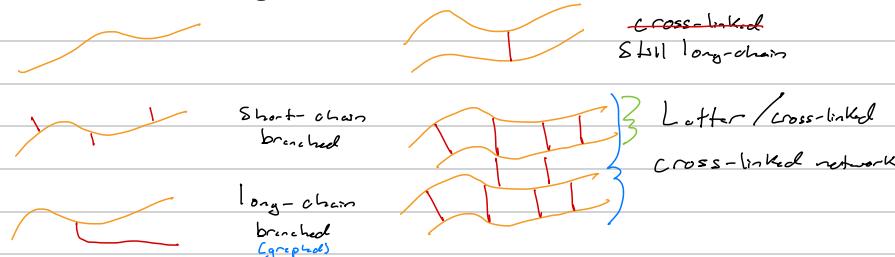
Not repeating

00 "

0△0 "

0△△0 Beginning of structure

Structure of Polymer Chains



Copolymers

- **AAAAAA** Mono polymer
- **AAAAAA BBBB** A,B-d block polymer
- **AAAAAA BBBB** graft polymers
- **A B A B A B A** alternating copolymer
- **A B B B A B A** 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

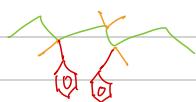
Conformation vs. Configuration

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°

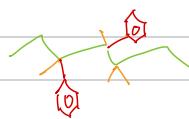
Configuration: Permanent structural difference caused during synthesis. Mild temp change does not affect this

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

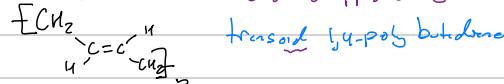
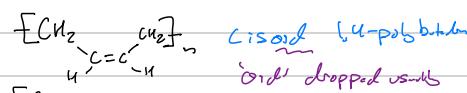
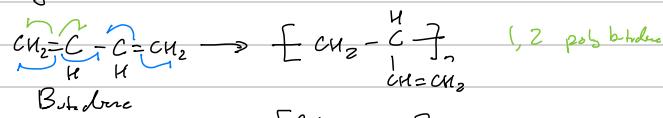
Can crystallize
↳ Material looks shiny

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

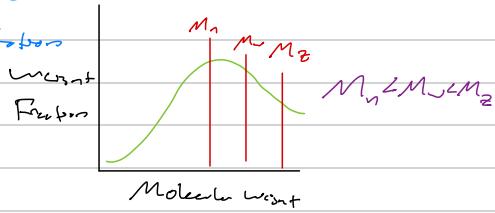
$$\text{Weight Avg MW: } M_w = \frac{\sum W_x M_x}{\sum W_x} \quad \text{How, } W_x = N_x M_x \rightarrow M_w = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

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 cyclohexyl ring

Materials Used: Polycyclic small oligomers of polycycles

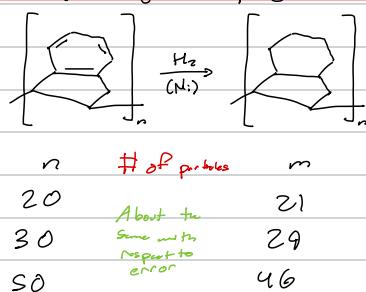
Meas Method: Colligative property Measurement



Discussed Degree Polymerization as the method was aggregate of molecules

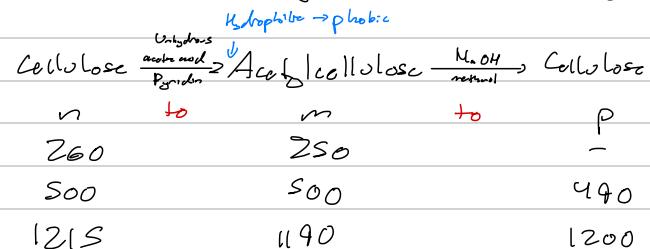
Staudinger's Experiments

Initial: Colligative Property Measurement



He was criticized for using small molecules

Final: Acetylation and regeneration of cellulose; viscosity measurement



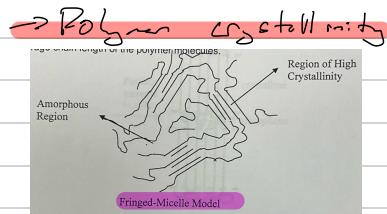
Directly from his paper, so viscosity value probably measurement error.

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

(like very cheap arm to make 'pamkin' lacquer)

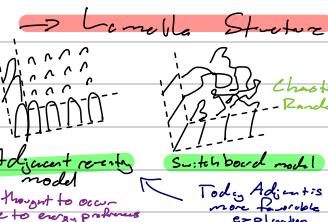
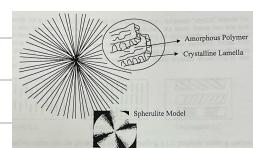
Morphology

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

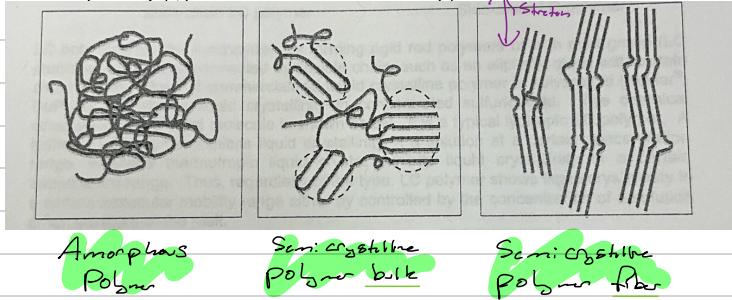


\rightarrow Spherulites

Polarized light reveals a molten cross (X)



Morphology Control: Stretching

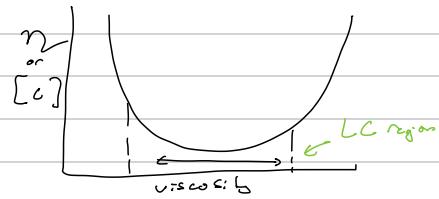


Stretching

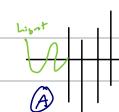
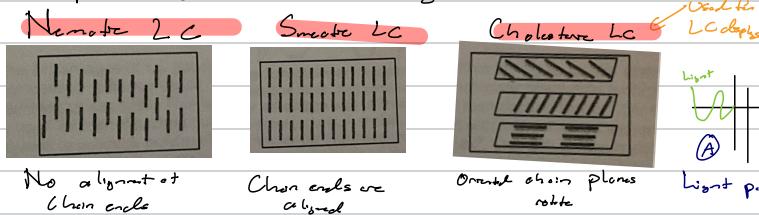
- Molecules realign along stretching direction.
- \uparrow stretching \rightarrow \downarrow intermolecular distance
 - \rightarrow leads to crystalline region formation
- Cracks are also observed along stretching direction
 - \rightarrow Thus the fibers or structural films are stronger along stretching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

Liquid Crystalline (LC) Polymers

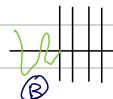
liquid = amorphous
crystal = perfectly ordered } Two opposing words used to express unusual material
that is neither completely amorphous nor ordered



Types of LC Polymers



vs.



Light passes through ① as it needs transverse alignment

Allows microwaveable

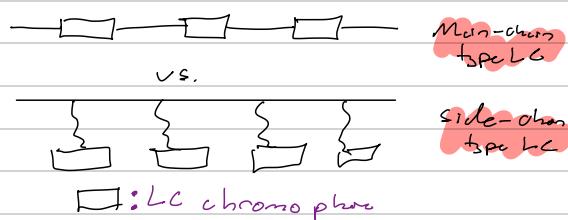
Supperware
only dissolving conc. sulfuric acid

Sustaining orientation
the layers so lighter
rotate up and out

Thermotropic LC: formed between certain temperature range
Lyotropic LC: formed between certain concentration range

ex: Aromatic Polyester

or Poly(p-phenylene phthalimide), polyaramid Kevlar



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



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!

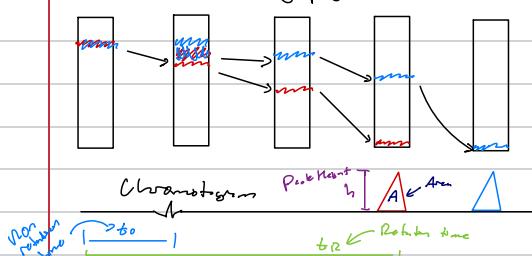
(ii) SEC (Size-Exclusion Chrom)

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

Can not 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

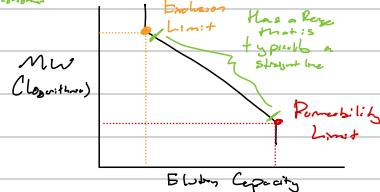
- Huge molecules come out first as small ones need to go through a lot of pores
- Uses cross-linked polystyrene → Created with vinyl aromatic monomers
 - ↳ This means most polymers will interact with the substrate

Separation Principle

→ Molecules $>$ Pore size cannot enter!

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

P.I. (monobrominated PDA)
UV (single/mixed/multiple wave lengths), 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

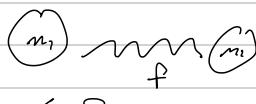
Model For Vibrational Spectroscopy

↳ 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 $m_1 r^2 = \frac{m_1 m_2}{m_1 + m_2}$ μ 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!

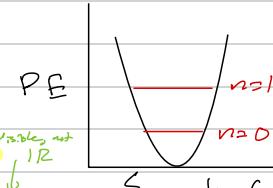
Analysis of Methylene Models



Potential Energy Diagrams

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

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



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
- Charge is 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

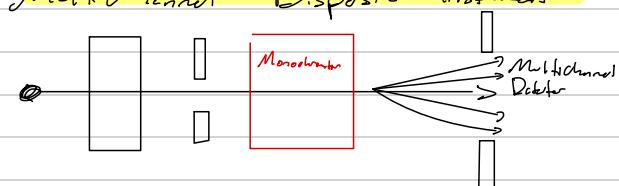
- H. Isidor: FT-IR analysis. Optical Techniques

Dispersive Infrared Instrument



Solution

Multichannel Dispersive Instrument

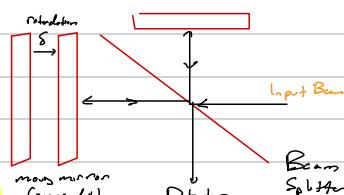


Disadvantages

- 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
- Carré: 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

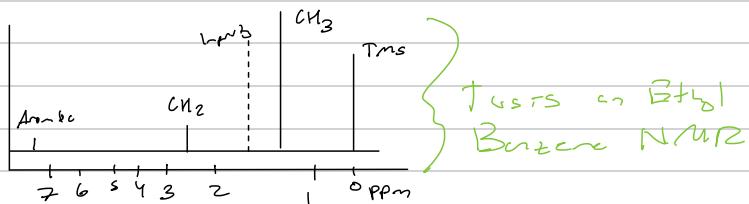
Disadvantages

- 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 - ν ps ~ one spot or. You can see impurities as well
- Farthest left are most ν ps, 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
- Modern Instrumentation consists of usually 4 ports

↳ 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 2nd order transitions & Thermograms
- ↳ With peaks, these are 1st order transitions

- Glass Transitions (second-order transition)

→ 2nd order transition

→ characterized by change in heat capacity

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

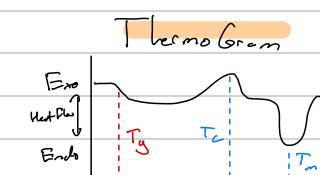
→ Small Endo peak may appear due to shippers / purity issues

- 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



temp →

Enthalpy relaxation
phenomenon



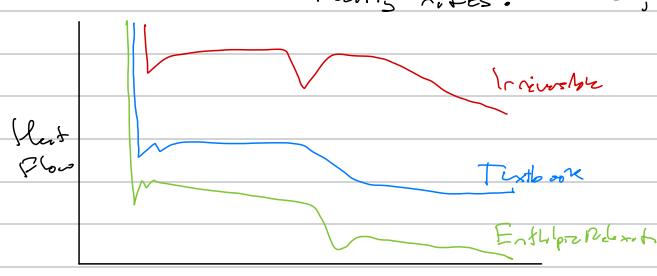
Reversing and Non-Reversing Contributions to Total DSC Heat Flow

$$\text{Total Heat Flow} \rightarrow \frac{dQ}{dt} = C_p \cdot \frac{dT}{dt} + f(t, T) \quad \begin{array}{l} \text{Non-reversible heat} \\ \text{component} \\ \text{Reversing eqn} \end{array}$$

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

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

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

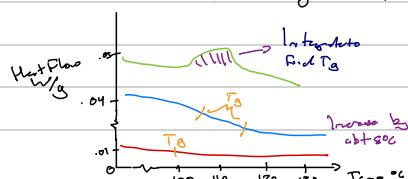


Reversible vs. Non-Reversible Transitions

Reversible: Glass Transition, melting

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

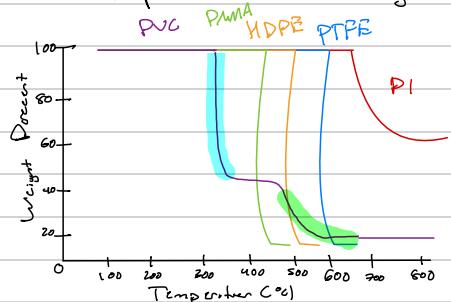
TMDSC Thermograms for Nanocomposites with 50 wt% of Polystyrene



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_d to me. Cannot probe chemical structure
 ↳ Allows you to study fragment structure when combined with structural analysis techniques

Example TGA Thermograms

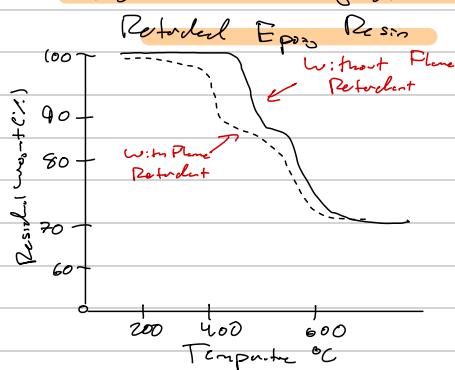


What's going on with PVC?

• 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_a

→ This Technique allows you to analyze the frequency of the activation energy changes

Activation Energy

TGA-based hygrothermal techniques

- TGA measures weight quantitatively
- TGA allows controlled decomposition
- Evolved gases are difficult to separate
- Real-time 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

Good Journals don't

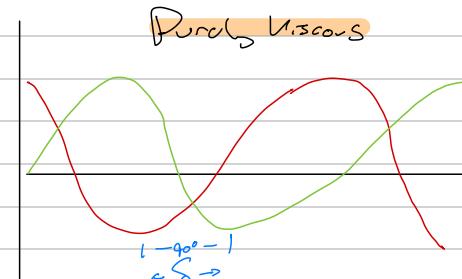
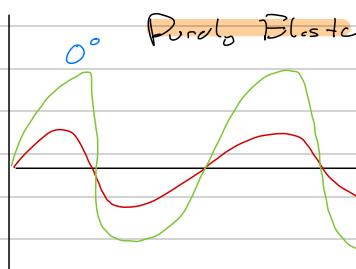
Accept single analytical result

melt & crystallization

Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA)

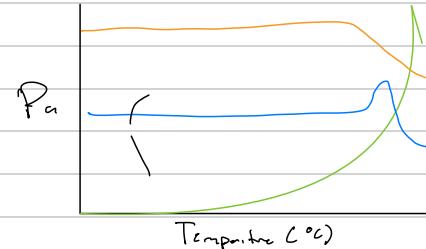
- Sample moves in sinusoidal motion instead of static/stress techniques
 - ↳ Bottom line: static stress actually changes the polymer structure
- Sinusoidal stress on a sample applied to measure stress in terms of phase lag
- You can learn:
 - (i) G' : storage modulus (recoverable energy)
 - G'' peak is $T_g \rightarrow$ (ii) G'' : loss modulus (irrecoverable energy lost as heat)
 - (iii) δ 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 δ (0°) true delay \rightarrow phase angle $\delta = 0^\circ$
- Purely viscous samples have a phase angle $\delta = 90^\circ$



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

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 rate of $G'' \rightarrow$ use $\tan \delta$
 T_g . Otherwise G'' peak is more rigorous to repeat

- DMA spectra compare 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 (gels)
- 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 accurate but useful for comparison)

Chapter 3



Goal: Polymer Physics

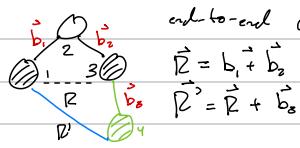
Plenty of equations will be discussed but not needed to memorize complex ones, included for explanation

↑ Simple equations are always better!!

Liquid Properties of Polymers

Single Chain Properties

End-to-end Distance



$$R = \sum_{i=1}^n b_i$$

end-to-end distance is given by R • Distance that connects two terminal atoms of the polymer chain

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

$$\vec{R}^2 = \vec{R} \cdot \vec{R}$$

• Poor solvent \rightarrow chain is tight and R is small

• Good solvent \rightarrow chains dispersed and R is large

• Polymer atoms move. Let's use $\langle R^2 \rangle$ for the average

$$\langle R^2 \rangle = \langle R \cdot R \rangle = \sum_{i=1}^n \langle b_i^2 \rangle + \sum_{i>j} \langle b_i \cdot b_j \rangle \quad n \text{ is number of bonds}$$

No Restriction in bond angle \angle measuring bond angle between atoms i & j

• Two average bond angles: $\langle \cos \theta_{ij} \rangle = 0$ \leftarrow cosine ranges from -1 to 1, so average is 0
 $\Rightarrow \langle R^2 \rangle = nb^2 \rightarrow R = b\sqrt{n}$ $\sum_{i>j} \langle b_i \cdot b_j \rangle = 0$

\angle is not very important for polymers

(Generally) Calculating number of bonds (n) given degree of polymerization (x_n): $n = 2x_n - 1$

Fixed Bond Angle

• Rotation around the bond is restricted but rotation must be constrained in a fixed angle range

$$\Rightarrow \langle b_i \cdot b_{i+1} \rangle = b^2 \langle \cos(\pi - \theta) \rangle = -b^2 \cos \theta$$

$$\therefore \sum_{i=1}^n \sum_{j=i+1}^n \langle b_i \cdot b_j \rangle = \sum_{i=1}^n \sum_{j=i+1}^n \langle b_i \cdot b_{i+1} \rangle$$

$$\Rightarrow \langle R^2 \rangle = nb^2 \left\{ \frac{1+s}{1-s} - \frac{2s(1+s)}{n(1-s^2)} \right\} \quad \text{where } s = \cos(\pi - \theta)$$

$$\cos(\pi - \theta) = -\cos \theta$$

Simplifying! $\frac{2s(1+s)}{n(1-s^2)} \approx 0$ for large n , so $\langle R^2 \rangle \approx nb^2 \left(\frac{1-\cos \theta}{1+\cos \theta} \right)$

$$\theta = 109.28^\circ \text{ for tetrahedral C-C bond, so } \cos \theta = -\frac{1}{2}$$

$$\Rightarrow \langle R^2 \rangle = nb^2 \left(\frac{\frac{1+\frac{1}{2}}{1-\frac{1}{2}}}{1-\frac{1}{2}} \right) = nb^2 \left(\frac{\frac{3}{2}}{\frac{1}{2}} \right) = 2nb^2$$

$$\therefore R = \sqrt{2} b \sqrt{n} \quad \sqrt{2} \text{ times larger than unrestricted bond angle}$$

Bond Angle Rotation

Note that you add a factor considers more scenarios

$$\langle R^2 \rangle = nb^2 \left(\frac{1-\cos \theta}{1+\cos \theta} \right) \cdot \left\{ \frac{2 + \exp(\frac{\Delta E}{kT})}{3 \exp(\frac{\Delta E}{kT})} \right\} \quad \Delta E = \text{activation energy}$$

For k : Boltzmann constant

K for size molecule

R for molar values

Activation Energy: Molecule to climb to react.

affected by stereo hindrance & catalysts

Radius of Gyration

• Given by S , easier to measure than R as it is measured by a light scattering technique

$$S = \sqrt{\frac{1}{n} \langle R^2 \rangle} \quad g = \frac{\langle S^2 \rangle - \langle S \rangle^2}{\langle S^2 \rangle - \langle S \rangle^2} \quad \begin{array}{l} \text{g-factor used to evaluate} \\ \text{the degree of branching} \end{array}$$

• Radius of gyration is smaller in a poor solvent than in a good solvent

• Defined as the distance from the center of gravity to the chain segment

Solution Properties

Viscosity

• Polymer molecules in dilute solution exist in a ball-like structure with diameter being determined by radius of gyration \leftarrow depends on the interaction of the polymer molecules with the solvent

• When concentration of solution increases, the number of balls increase until they start interacting w/ each other & semi-dilute conc.

• In a concentrated solution, the polymer molecules don't exist as separate balls but instead have interact with each other \leftarrow polymer chains melt and are stretched

• A polymer chain is a good solvent of itself acting as a solvent of another chain

Solvent
Poor

Conc:
Temp:

Low Conc.
Low Temp.

Light \rightarrow Medium

Med Conc.
Med Temp.

Good

High Conc.
High Temp.

Polymer acts
as a solv.
Br. itself

High Conc.
High Temp.

Viscosity influenced
heavily in good
solvent

- Viscosity: Difficulty to flow, given by η

$$\eta = \eta_0 (1 + a_1 C + b_2 C^2 + \dots)$$

solvent viscosity
Concentration of polymer molecules
Coefficient for terms related to prop. of individual polymer chain
Cb related to the polymer-solvent interaction

- Reciprocal is test of viscosity/flow

$$\lim_{C \rightarrow 0} \frac{\eta - \eta_0}{\eta_0 C} = a_1 = [\eta] \leftarrow \text{This is intrinsic viscosity}$$

(Benesch coefficient, D_{B_1})
versus molar mass M_w

Extrapolant

Extrapolate to $C \rightarrow 0$, higher order terms can be ignored

- Relative Viscosity: $\eta_r = \frac{\eta}{\eta_0}$
- Einstein: viscosity of any dilute solution with spheres: $\eta = \eta_0 (1 + 2.5 \phi)$

- Mark-Houwink-Kirkwood Equations: $[\eta] = K M^\alpha$ for $0.5 \leq \alpha \leq 0.8$

Molecular weight \rightarrow Viscosity \downarrow
Molecular weight \rightarrow Viscosity \downarrow
Molecular weight \rightarrow Viscosity \downarrow

↑ Polydispersity
↑ Limit Eq.
holds for lowest concentrations

- Plastic fillers are very influential on increased viscosity.

Thermodynamics of Polymer Solutions

- Gibbs free energy provides extra energy that can be utilized

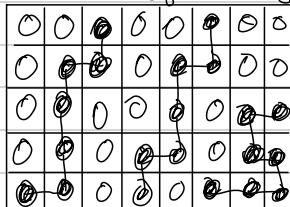
- Thermodynamic properties of interest result in a conversion of mixing the polymer into the solvent

- $G = H - TS = U + PV - TS$ Flory-Huggins calculated ΔS from a lattice model

\uparrow Gibbs free energy \uparrow enthalpy of mixing \uparrow entropy of mixing

- Phase equilibrium, osmotic pressure, vapor pressures, and other thermodynamic properties can be studied to obtain thermodynamic factors of the polymer solution

Flory-Huggins Theory



- Every lattice point is either occupied by a solvent molecule (open circle) or closed circle (chem. repeat)
- Number of possible shapes chains can take is the entropy
- Percentage of lattice that is repeat units determined by molecular weight
- Requires assumptions to simplify, which makes it a semi-quantitative model
- For the calculations/derivations to work assumptions

Assumptions (i) A polymer solution can be regarded as channel repeat units of the polymer chains

Occupying each lattice unit

(i) is subject to → (ii) The lattice unit has equal size and each lattice unit can be occupied either by a solvent molecule most entropically or the chemical repeat unit

is being actively maintained (iii) The number of the neighboring chemical repeat units called the volume number

(iv) The number of N_2 polymer chain in N_1 lattice units, $w(N_1, N_2)$ provides entropy

ΔS uses the Boltzmann equation: $\Delta S = k \log w(N_1, N_2)$.

• The entropy of mixing can be described as $\Delta S = R(\Phi_1 \log \Phi_1 + \frac{\Phi_2}{m_2} \log \frac{\Phi_2}{m_2})$ Soft & hard express F is used to describe the volume fraction

• Solvent/solvent interaction energy given as ϵ_{11}

• Solvent/channel repeat unit II given as ϵ_{12}

• Channel repeat unit/channel repeat unit II given as ϵ_{22}

• Therefore enthalpy of mixing H can be expressed as: $\Delta H = Q_{12} \Delta \epsilon_{12}$

↳ { where Q_{12} is the number of contacts between solvent molecule and the channel repeat units
 $\Delta \epsilon_{12} = 0.5(\epsilon_{11} + \epsilon_{22}) - \epsilon_{12}$

• Can now get free energy of mixing ΔG

$$\Delta G = RT(\Phi_1 \log \Phi_1 + \frac{\Phi_2}{m_2} \log \frac{\Phi_2}{m_2} + X_{12} \Phi_1 \Phi_2)$$

where $X_{12} = \frac{\sum \Delta \epsilon_{12}}{kT}$

* m replaced by number avg
molecular weight M_n
or $\frac{M_w}{M_n}$ for polymer blend

Cannot theoretically be negative but $X_{12} < 0$ has been found experimentally

Florey-Huggins
Parameter

Φ -solvent is
 $X_{12} = 0.5$ exactly

$X_{12} < 0.5$ is good solvent. $X_{12} > 0.5$ is bad solvent

Floeg-Huggins Theory Continued

Advantages: (i) Equation is quite simple

(ii) well corresponds to small molecular weight compound

(iii) m_1 and m_2 can be used to describe polymer blends

Disadvantages: (i) $\Delta V = 0$ by their assumption as each Lattice units occupied entirely by solvent molecule or chain repeat unit

(ii) The fixed lattice size does not allow to evaluate thermal expansion

Big Disadvantage: (iii) The same lattice size does not evaluate the different size of the solvent and chain repeat unit

Colligative Properties

Vapor Pressure

• Vapor pressure lowering can be used to measure molecular weight of polymers

• Activity Coefficient γ can be ignored if the solution concentration is ultradilute

$$\alpha_1 = \frac{P_1 \gamma_1}{P_1^0 \gamma_0} \approx \frac{P_1}{P_1^0} \rightarrow \text{ideal solution assumption: } \alpha_1 = 1 \rightarrow \frac{P_1}{P_1^0} = 1 - \frac{N_2}{N_1} \quad \begin{cases} 1: \text{solute} \\ 2: \text{solute} \end{cases}$$

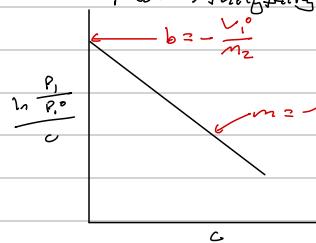
activity γ
of the solution

• 1 cc of solution with c grams of solute & w_1 grams of solvent: $\frac{N_2}{N_1} = \frac{c}{w_1/m_2}$

• $V_1 + V_2 = 1$ in 1 cc solution

$$\text{Linearized Equation: } \frac{\ln \frac{P_1}{P_1^0}}{c} = - \left(\frac{V_1^0}{M_2} \right) - \left\{ \frac{V_1^0}{M_2 P_2} + \frac{(V_1^0)^2}{2 M_2^2} \right\} c + \dots \quad \begin{cases} \text{Can ignore terms due} \\ \text{to a basis to so Taylor expansion} \\ \text{higher terms} \rightarrow 0 \end{cases}$$

• Plot Analytically



$$\ln \frac{P_1}{P_1^0} < 0 \quad \text{for} \quad \frac{P_1}{P_1^0} < 1, \quad \frac{V_1^0}{M_2} > 0$$

\downarrow what we know after

\downarrow Simple measure P_2 or V_1^0 of polymer

\downarrow Density is quite accurately measured (4-5 significant figures)

• we assumed solution to be ultradilute \rightarrow greatly simplifies equations but reduces effectiveness

Osmotic Pressure

• ΔG increases upon mixing polymer with a solute: Osmotic pressure is the pressure needed to equalize pressure on semipermeable membrane as a result of this

Factors that determine equilibrium?

(i) Various porosity of membranes

(ii) Area of the membrane

(iii) Size distribution of capillaries

(iv) Viscosity of the solvent

(v) Distance from the equilibrium

Advantages

(i) Simple measurement

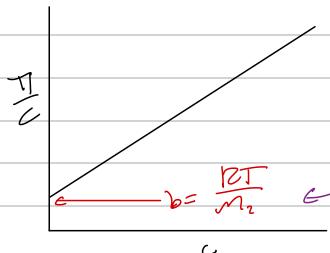
(ii) inexpensive device

Disadvantages

(i) Takes a long time to approach equilibrium

(ii) Solute absolute solution

(iii) A true semipermeable membrane is rarely available



$$\frac{\Pi}{c} = \frac{RT}{M_2} + RT \left(\frac{1}{M_2 P_2} + \frac{V_1^0}{2 M_2^2} \right) c$$

c

\downarrow Used now as if you can get intercept, then you can easily get M_2

Solid State Properties

The Rubber Elasticity Theory

- Unique property of polymers is rubber elasticity
 - Crosslinked rubber can maintain elastic deformations at very large strain
 - Rubber elasticity characterized by a large deformation and extremely low modulus
 - Material can deform many times that of its original length
 - Modulus proportional to rigidity of a material. Natural Rubber modulus $E \approx (0.3, 1.5) \text{ MPa}$
- \hookrightarrow elastomers are extremely pure and strong with modulus $\approx 500,000 \text{ MPa}$

$$dU = T dS - P dV + f dx$$

Rubber volume
total energy
stretches by dx @ applied force F

From $F = U - TS$, Helmholtz's free energy: $dF = dU - T dS - SdT$

Limited to slightly crosslinked systems such as rubbers.

$$\Rightarrow f = \left(\frac{\partial U}{\partial x} \right)_{V,T} - T \left(\frac{\partial S}{\partial x} \right)_{V,T} \quad \& \quad \left(\frac{\partial F}{\partial T} \right)_{V,x} \approx \left(\frac{\partial P}{\partial T} \right)_{V,x} \xrightarrow{\text{Elastic}} \Rightarrow f = -T \left(\frac{\partial S}{\partial x} \right)_{V,T} \quad \& \quad f = T \left(\frac{\partial P}{\partial T} \right)_{V,x}$$

Momentary change $\approx 0^\circ$ static

positive; increasing temperature causes forces to increase

- Strain induced crystallization: Limits elasticity exhibited upon stretching. Happens only in tension.
- DMA plot of G' vs. T shows rubbery plateau for thermosetty polymers

Pure Thermodynamic Transitions should not be rate dependent

Glass Transition Temperature

Structure Independent Concept?

- Joint theory of Thermodynamics & kinetics is favorable, but is not published yet \hookrightarrow current shorthand
- Aggregates state of a material changes by changing T & P of the material
 - \hookrightarrow Vapourization, melting, and freezing called phase transitions
- Ehrenfest with order thermal transition
 - \hookrightarrow Gibbs free-energy differential: $(n-1)^{\text{th}}$ is ots, n^{th} is disots.

Example: molts, evaporation are disots. with respect to V and S

T_g is second or dual disots. with respect to heat capacity which is a second derivative of G.

- Amorphous Polymers experience spec. for volume change only at T_g \hookrightarrow No melting for amorphous polymers
- Semi-crystalline polymers experience spec. for volume change first at T_g , then at T_m
- T_g can be easily observed by measuring quantities like:

Thermal expansion coeff., heat capacity, refractive index, diffusion coefficient, dielectric constant, and modulus

Free Volume Theory for T_g

- Free Volume: The volume where polymer chains can freely move around
- Occupied Volume: The space where the molecular chain itself occupies \hookrightarrow can be expressed

$$f = f_g + \alpha_f(T - T_g) - \beta_f P$$

$\bullet T_g$ is temperature at which free volume coefficient = $25\% = 0.025$

Fox Equations

- For multi-component systems with weight fractions (w_i) and T_g values ($T_{g,i}$):

General Fox Equations: $\frac{1}{T_g} = \sum_{i=1}^n \frac{w_i}{T_{g,i}}$ Originally proposed as $\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}$

\hookrightarrow Applicable strictly to molecularly miscible blends!

Compatible & Miscible: miscible is thermodynamically, while compatible is a loose engineering term
Flawed as thermal expansion coefficient is not considered

Glass Transition Temperature Continued

Gordon-Taylor Equation for Polymer Blends

- $B_p P \approx 0$ for incompressible solids
- Let $K = \frac{\alpha_{f_2}}{\alpha_{f_1}}$

$$T_g = \frac{T_{g,1} + (KT_{g,2} - T_{g,1})\phi_2}{1 + (K-1)\phi_2}$$

$\hookrightarrow K$'s ratio of thermal expansion coefficient of polymer 2 to polymer 1

Polymer	T _g (°C)	Polymer	T _g (°C)
Polyethylene	-125	Nitrocellulose	53
Polydimethylsiloxane	-123	Nylon-66	50
Polybutadiene	-90	Nylon-6	50
Polyisobutylene	-70, -60	Poly(ethylene terephthalate)	69
Polyoxymethylene	-50 (-85)	Poly(vinyl alcohol)	85
Poly-1-pentene	-40, -24	Poly(vinyl chloride)	87
Poly(vinylidene fluoride)	-35	Poly(vinylidene)	100
Poly-1-butene	-25	Poly(methyl methacrylate)	45 (isotactic) 105 (syndiotactic)
Poly(vinyl fluoride)	-20, -73	Polyacrylonitrile	104
Polypropylene	-18, -10	Poly(vinyl formal)	105
Poly(vinylidene chloride)	-17	Triacetylcellulose	105
Poly(methyl acrylate)	3	Poly(carbonate)	130
Poly(vinyl acetate)	29	Poly(α -methyl styrene)	167
Poly(chlorotrifluoroethylene)	45		

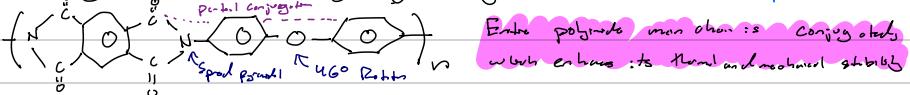
- As the rigidity of the chemical repeat unit increases, T_g increases

T_g increases

- Very wide range of T_g, some exceed 500°C

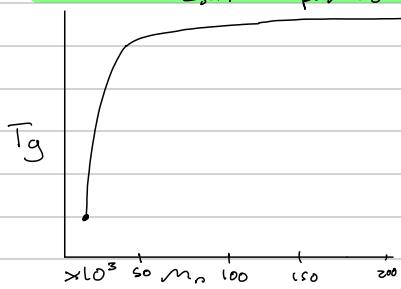
- Proportional to mobility of chain

- Polyimide (Kapton); very high T_g used to isolate compatibles



Entire polymer main chain is conjugated which enhances its thermal and mechanical stability

Molecular weight Dependence on T_g & T_m



- T_g plateaus starting at ~50,000 molecular weight
- Smaller molecular weights have greater thermal perturbation contribution
- During melting, both liquid and solid phase coexist
- $\Delta H \geq 0$ @ equilibrium $\Rightarrow T_m = \frac{\Delta H_m}{\Delta S_m}$ but entropy is hard to measure
- Melting is quite abrupt and unique of the solid for material characterization and checked for purity
- Flory's Proposal: $\frac{1}{T_m} - \frac{1}{T_g} = \frac{2R\ln b}{\Delta H_m M_n}$

T_m^0 : melting point of ∞ MW
b: G.S. const.
 ΔH_m : heat of melt 1 mol./Repeating

- Melting is first order transition, discontinuous transition
- Boyer-Beaman Rule

$$(i) \text{ For symmetric molecules: } T_g = \frac{1}{2} T_m \quad \left. \begin{array}{l} \text{Absolute temp.} \\ \text{not } ^\circ\text{C} \end{array} \right\}$$

$$(ii) \text{ For asymmetric molecules: } T_g = \frac{2}{3} T_m$$

Mechanical Properties

Stress

$$\sigma = \frac{P}{A_0}$$

Load / initial cross section

$$\epsilon = \frac{\Delta L}{L_0}$$

original length / original length

This is the engineering stress

Strain

$$\epsilon = \frac{\Delta L}{L_0}$$

original length / original length

Flexibility

Modulus

$$E = \frac{\sigma}{\epsilon}$$

(Young's modulus)

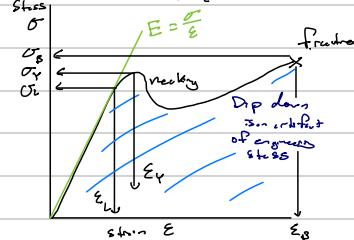
Expresses rigidity

True Stress

Cross-sectional area changes with true ϵ , so it is difficult to measure continuously. Use only when desired

Young's Modulus = σ/ϵ ; Shear Modulus = $G = \tau/\epsilon$

Stress - Strain curve



$$E = \frac{\sigma}{\epsilon}$$

Fractional E: $E = \int_0^{\epsilon} \sigma d\epsilon$

- A polymer first deforms linearly \Rightarrow Elastic behavior
- The first point that deviates from linearity \Rightarrow Lower yield stress
- Local maximum upper yield strain
- Poisson's Ratio: $\nu = \frac{\Delta d}{\Delta l}$

\hookrightarrow a negative ratio means anisotropic materials like graphite or honeycomb

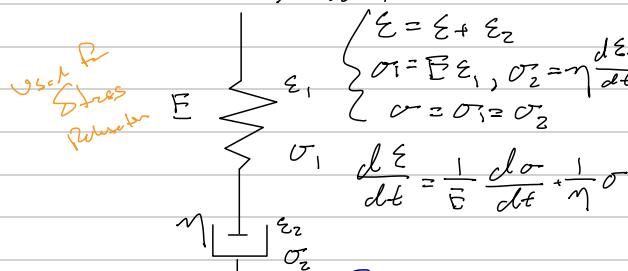
Theoretical Poisson Ratio of Ideal Rubber is 0.5

Viscoelastic Properties

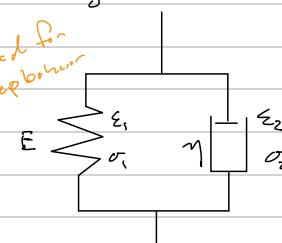
ideal elasto material: completely recovers from deformation

ideal viscous material: Flow is a constant shear stress rate which is proportional to the applied stress

Maxwell Model

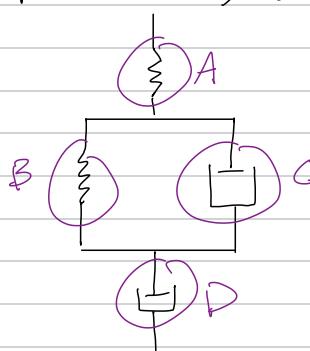


Motz Model

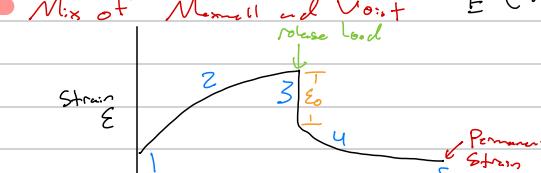


Exponential Growth

For Element Model Mix of Maxwell and Motz: $\epsilon(t) = \frac{\sigma_0}{E} \left(1 - e^{-\frac{E}{\eta} t} \right)$



Exponential Decay



Point-model

1. A spring is elasto component

2. B, C, & D for two elasto, D for driving force
constant strain recovery

3. A

4. B + C, no weight \rightarrow no external drag forces on initial point (B)

5. D, permanent deformations on D as external drag force removed

C follows B's movement

Dynamic Mechanical Analysis

Apply sinusoidal strain $\epsilon(t) = \epsilon_0 e^{i\omega t} \Rightarrow \sigma(t) = \frac{1}{1-i\omega/E} \epsilon(t)$ i is angular frequency

Property	Parallel	Series
Stress	σ	ϵ
Strain	ϵ	γ
Modulus	E	G

$$\Rightarrow \sigma(t) = G * (i\omega) \gamma(t)$$

use different symbols for different parts

can calculate E from G or G from E if Poisson's ratio is known for the material

$$G * (i\omega) = G'(\omega) + i G''(\omega)$$

$$\Rightarrow \tan \delta = \frac{G''}{G'}$$

loss tangent or loss factor, usually

plotted for a solid sample as function of temperature

Smaller, but Important, Topics

Time-Temperature Superposition Principle

Viscoelastic properties are important to material design. Often desired that a property at a certain T is predicted after a prolonged period of time. Unfortunately tests take is highly limited so that actual data is not available.

WLF Equations

- TTS Principle allows predicting properties at true T without performing an actual long-term experiment

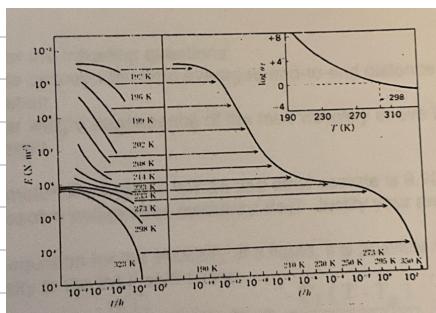
Higher T
Temperature \Rightarrow shorter time to achieve the same structural change

- Use Williams-Landel-Ferry Equation to calculate shift factor along a log scale

$$\log_{10} \alpha_T = \frac{-8.86(T - T_g)}{101.6 + (T - T_g)}$$

where T is test temperature on the curve

where T_g is temperature where you want to use test data



- Master curve created by Prof. Ferry
- α_T can be used to better reproduce the master curve
- Predict Property
 - \hookrightarrow Go to true or α_T
 - \hookrightarrow Line up with complete set of curves
 - \hookrightarrow ideal, but not realistic to estimate non-ideal accidents
- Sometimes T_g is used for T_0 , which can change numbers dramatically
 - \hookrightarrow just something to look out for in real-world applications

Viscosity

- Resistance to acceleration of the fluid
- Elasto property of rubber is already described to be entropic
- Viscosity related to diffusion coefficient described by Einstein equation:

$$\eta = \frac{kT}{3\pi a D} \quad \text{where } D: \text{diffusion coefficient}$$

a : a value similar to the molecular size

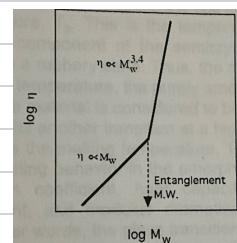
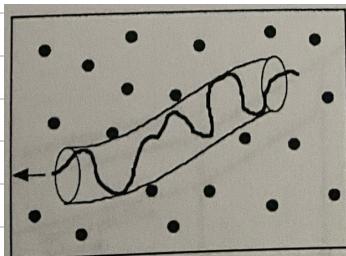
Reptation Model

- Entanglement MW: Somewhat dependent on molecular structure rigidity.

\hookrightarrow Not observed with pure crystalline polymers

\hookrightarrow Not a clear dependence on degree of polymerization

- Doohlitt's Equation: $\log \eta = \log A + \frac{B}{P(T)}$ where $P(T)$ is temperature dependent viscosity



Polymer	Entanglement Molecular Weight	Degree of Polymerization (Xn) at Entanglement MW
polyethylene	4,000	140
cis-1,4-polybutadiene	7,000	130
cis-1,4-polyisoprene	14,000	210
polyisobutylene	17,000	300
polydimethylsiloxane	29,000	390
polystyrene	35,000	340

Hildebrand Solubility Parameter

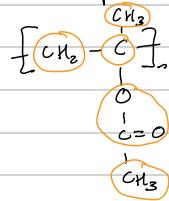
$$\delta = \frac{\sum F^*}{\sum V^*} \quad \text{where } F^* = \text{molar attraction contribution}$$

V^* = molar volume contribution

• F^* and V^* are empirically derived and not really something you could go experimentally measure

• You can measure δ experimentally without referring to eq.

Example - PMMA



Groups

$$\delta = \frac{132 + 2(31.8) - 97 + 248}{16.5 + 2(31.8) - 14.8 + 19.6}$$

$$= \frac{769}{84.9} = 9.06 \quad \text{Slightly hydrophobic}$$

Group structure	Molar volume contribution, V^* ($\text{cm}^3 \text{mol}^{-1}$)	Molar attraction contribution, F^* ($[\text{cal} \cdot \text{cm}^3]^{1/2} \text{ mol}^{-1}$)
-CH ₃	31.8	218
-CH ₂ -	16.5	132
>CH-	1.9	23
>C<	-14.8	-97
C≡H ₃	41.4	562
C≡H ₂	58.5	652
C≡H ₁	75.5	735
CH ₂ =	29.7	203
-CH=	13.7	113
>C=	-2.4	18
-OCO-	19.6	298
-CO-	10.7	262
-O-	5.1	55
-Cl	23.9	264
-CN	23.6	426
-NH ₂	18.6	275
>NH	8.5	143
>N-	-5.0	-3

written & O.S. of
measured value

Measured value is 9.19

Chapter 4



Goal: Study Polymer Chemistry & Synthesis

Step & Addition Polymerization

Classification of Polymerization

- Most common classifications are Addition and Step Polymerization

↳ more than two exist, and there are sub-classifications of these

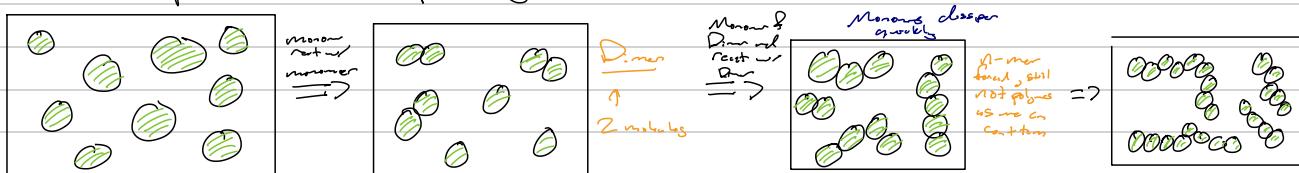
Step Polymerizations

↳ Step-growth polymerization

- Condensation polymerization & alkene polymerizations
- Polyaddition polymerization
 - No coinitiator
 - No solvent
 - Water formed as product (HCl or H₂O)

Characteristics of Step Polymerization

Schematic Representation of Step Polymerization



Only 1 chain from template but many different molecular weights

- Growth by the reaction of c. two oligomers
- Chain ends remain reactive
- Rapid loss of monomer species (first reaction produces a dimer)
- Molar mass initially increases slowly and then quickly towards the end of the reaction
- At c. step 50 a range of molecular species are present
- No initiator is necessary, but can be helpful sometimes
- Driving force of the reaction can be the removal of the condensation product

Also see Rn
Polymerizations

Carothers Theory

$$\text{number of particles initially} \times_n = \frac{\text{No. of particles initially}}{\text{No. of molecules at time t}}$$

$$\text{Let } p = 1 - \frac{N}{N_0} \text{ and thus } \frac{N}{N_0} = 1 - p \Rightarrow \frac{\text{No. of particles initially}}{1-p} = \frac{1}{1-p} \times_n = \frac{1}{1-p}$$

$$X_n = \frac{M_w}{M_w + M_n}$$

How do we report? $\frac{M_w}{M_w + M_n}$
polymers -> monomers

• Only applicable for stoichiometric polymerizations! How do we know? Use FT-IR, NMR, MS, SEC, DMA, etc

Molecular Weight Products for non-stoichi polymerization

- Reactant ratio: $r = \frac{N_A}{N_B}$ such that $r < 1$ ratio must always be less than 1!
- For linear molecules with two functional groups per molecule $N_0 = \frac{N_A + N_B}{2}$, sub $N_A = r - N_B$
- $\therefore N_0 = \frac{N_B}{2}(1+r)$

- Defn ext. of reactants in terms of number of unreacted groups of A or B after time t

$$(i) \text{ Unreacted A} = r N_B (1-p) \quad (ii) \text{ Unreacted B} = N_B (1-rp)$$

$$\text{and thus } \# \text{ unreacted total molecules: } N_t = \frac{r N_B (1-p) + N_B (1-rp)}{2} = \frac{N_B (1-r-2rp)}{2}$$

\hookrightarrow Substitute this N and $N_0 = \frac{N_B (1+r)}{2}$ into $X_n = N_0/N_t$ to get

General Carothers Eqn: $X_n = \frac{1+r}{1+r-2rp}$

For r=1 we have $X_n = \frac{1}{1-p}$

Characteristics of Free Radical Polymerization

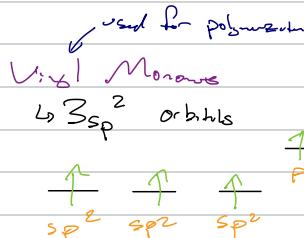
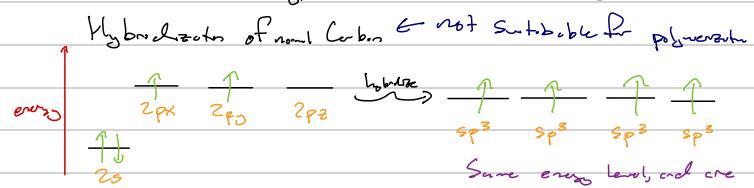
• 3 Key steps:

(i) Initiators

(ii) Propagation

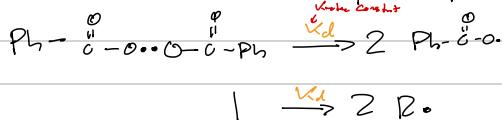
(iii) Termination

Matured of Bond: Electron Orbital Structure



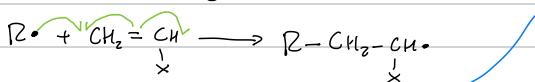
Initiators

(i) Process 1: Initiator molecule splits to produce free radicals

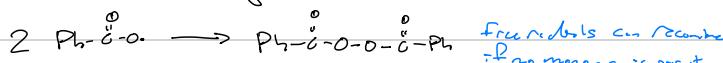


Second step reacts with
other free radical
reactor or monomer molecule

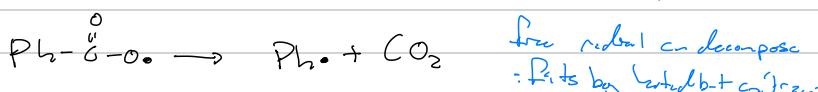
(ii) Process 2: Attacks monomer



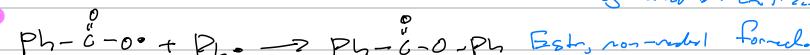
→ Initiator efficiency: f_{cl}



or



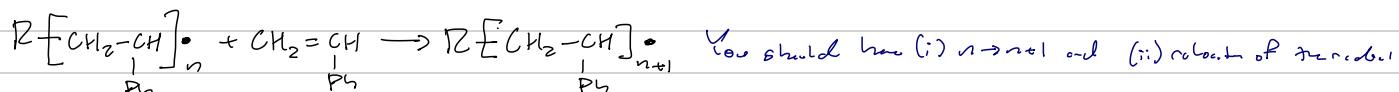
then



or



Propagation

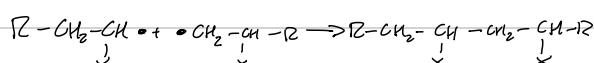


Successive repetition of new monomer being added to free radical chain to create a longer polymerization

Termination

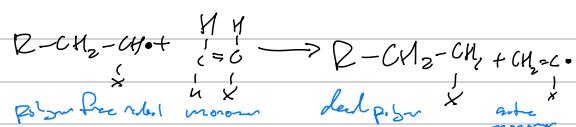
An overall reaction that is going to consume a radical species

Termination 1) Collided Combination (coupling)

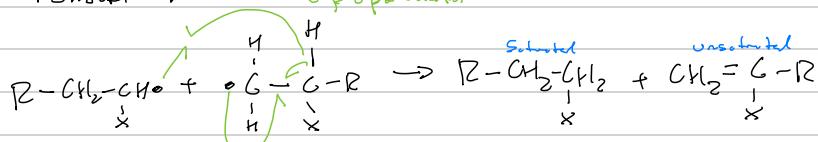


Generally: $R\cdot + R\cdot \xrightarrow{heat} \text{Product of two radicals}$

Termination 3) Collided Chain Transfer



Termination 2) Collided Disproportionation



Characteristics

- Initiator is almost always necessary

- Initiator molecule must be activated

- Absorb initiator combs with monomer

- Relatively slow loss of monomer spaces

- As soon as active monomer

- is produced, molecular weight with monomer

- polymer stats increasing rapidly

- Large molecular weight polymer chains coexist

- is produced, molecular weight with monomer

- Active chain ends die at end of the polymerization

Kinetics of Free Radical Polymerization

- The 3 steps can be expressed by the following

$$\text{Rate of initiation: } R_i = 2fK_d[I]$$

f = initiation efficiency (also probability constant of the initiator)
 K_d = rate constant for initiation

$$\text{Rate of propagation: } R_p = K_p[M][P_{n^*}]$$

K_p = rate constant of propagation

$$\text{Rate of Termination: } R_t = K_t[P_{n^*}]^2$$

K_t = rate constant for termination

→ 4 variables and 3 equations

Assume: Steady-state assumption, so $R_i = R_t$, thus rate of initiation is the same as rate of termination

$$R_i = R_t \Rightarrow 2fK_d[I] = 2K_t[P_{n^*}]^2$$

Free radical constants at any instant cannot be experimentally determined w/ today's techniques, use overall constants!

$$\text{so } [P_{n^*}] = \left(\frac{fK_d[I]}{K_t} \right)^{1/2}$$

Substitute $[P_{n^*}]$ into rate of propagation

$$\text{thus } R_p = K_p \left(\frac{fK_d}{K_t} \right)^{1/2} [I]^{1/2} [M] = K [I]^{1/2} [M] \quad \text{where } K \text{ is combination of all constants}$$

Kinetic Chain Length

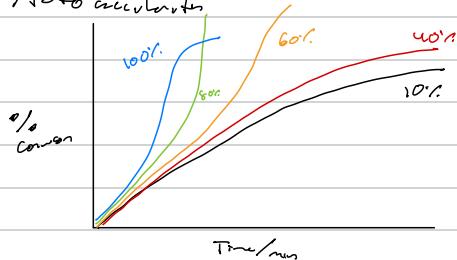
$$\text{Defined as } \bar{n} = \frac{R_p \text{ rate of prop.}}{R_i \text{ rate of init.}} = \frac{K_p [M]}{2(fK_d K_t)^{1/2} [I]^{1/2}} = K' \frac{[M]}{[I]^{1/2}}$$

Related to average degree of polymerization as:

$$\textcircled{1} \bar{x}_n = \bar{n} \text{ for termination by disproportionation} \quad \textcircled{2} \bar{x}_n = 2\bar{n} \text{ for combination (coupling)}$$

$$\text{Thus, } \begin{cases} \text{Increase in } [\text{monomer}] \Rightarrow R_p \uparrow, \bar{x}_n \uparrow & \text{More monomer for same amount of initiator} \\ \text{Increase in } [\text{initiator}] \Rightarrow R_p \uparrow, \bar{x}_n \downarrow & \text{More initiator for same amount of monomer} \end{cases}$$

Autoacceleration



out of control when autoacceleration happens

• polymerization exothermic heat is released and initiator takes it in to decompose

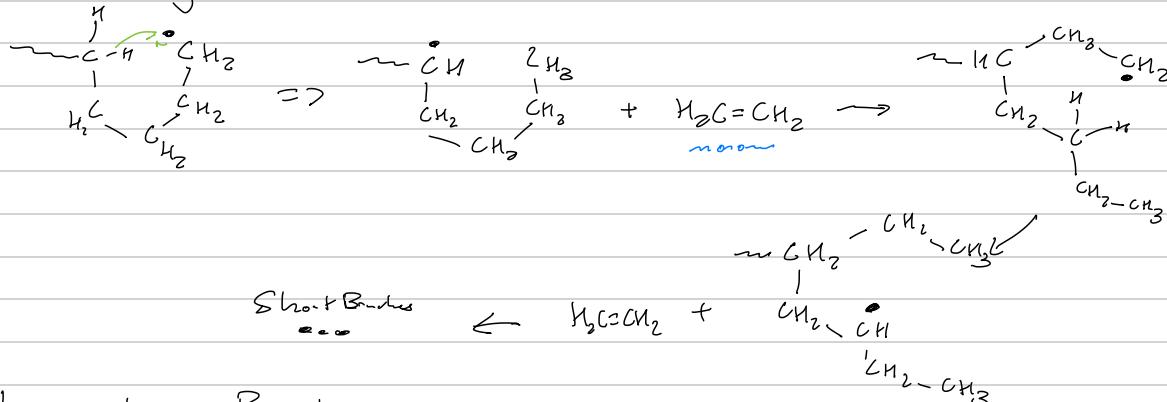
• used to be called (i) Transient RP-Norrish effect, (ii) Norrish effect, (iii) Grl effect, and now (iv) Autoacceleration

- As the content of large polymer molecules increases with reaction time and the polymer solution viscosity goes, the viscosity of the solution dramatically increases
- The mobility of the polymer chain radicals nearly halts and hence K_p is reduced substantially due to the low diffusional rates of the polymer free radicals in such viscous media. In the meantime, the initiator molecules continue to split. The steady-state condition no longer holds!
- The small monomer molecules can easily diffuse to the polymer free radicals as well as the usual initiator free radicals
- Thus, from the overall rate equation, a reduction in K_p increases both R_p and \bar{x}_n

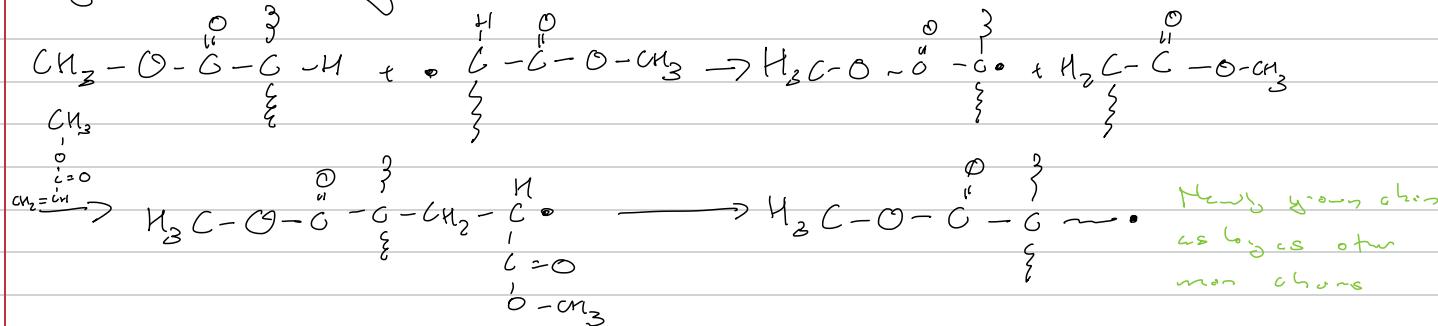
Chain Transfer

Chain transfer occurs when one polymer chain is terminated but a new growing chain is initiated. Thus, the total free radical concentration does not change. This is different from a termination reaction in which all free radicals are consumed. There are two main types of chain transfer: intramolecular charge transfer (backbiting) and... Page 70 instead

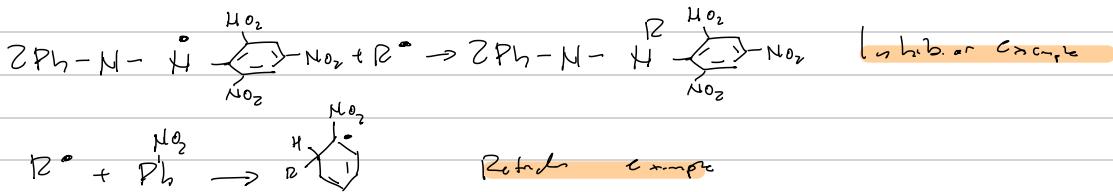
Back Bitting



Long Chain Branching



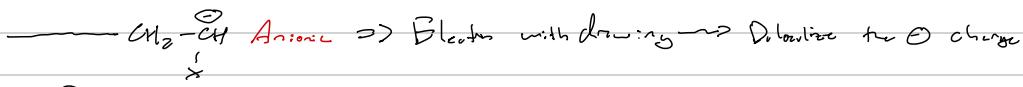
\rightarrow Initiators and
Radicals and
Chain transfer
agents



Ionic Polymerization

Part of Addition-Caten chain/chain-growth polymerization

- Delocalizing the charge will stabilize it, and thus the life time of the active species live longer



Cationic Polymerization

(i) Initiators

- Creation of \oplus cation centers: Monomer + electrophiles R^{\oplus} .

a) Protonic acids, H_2SO_4 : perchloric acid, HClO_4 , involve addition of H^+ to monomer \rightarrow strong acids good

b) Hydrogen halide acids, HCl not suitable because Cl^- recombines \rightarrow too much

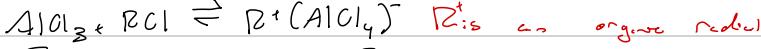
c) Lewis acids + co-catalyst such as inorganic or organic halide \rightarrow Good, but need a co-catalyst

\rightarrow Boron trifluoride, BF_3

\rightarrow Aluminum chloride, AlCl_3

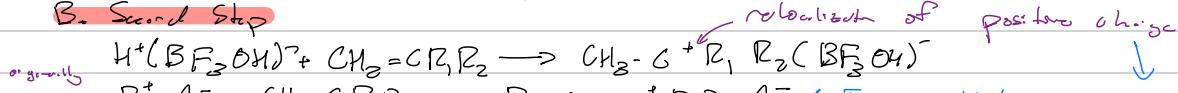
\rightarrow Tin tetrachloride, SnCl_4

A. First Step \rightarrow must be added carefully in p.-fit + stoichiometric conditions



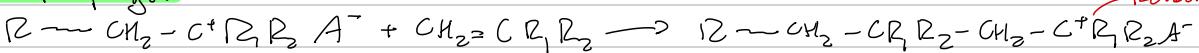
\bullet First step is creation of positive charge!

B. Second Step

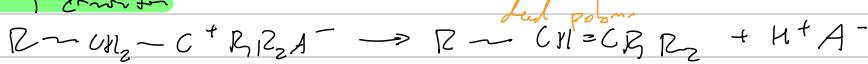


$\text{B}^+ \text{A}^- + \text{CH}_2=\text{CR}_1\text{R}_2 \rightarrow \text{R}-\text{CH}_2-\overset{\oplus}{\underset{\text{Ph}}{\text{C}}} \text{R}_1\text{R}_2 \text{A}^- \downarrow$ This is able to react with another monomer

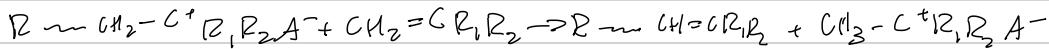
(ii) Propagation



(iii) Termination

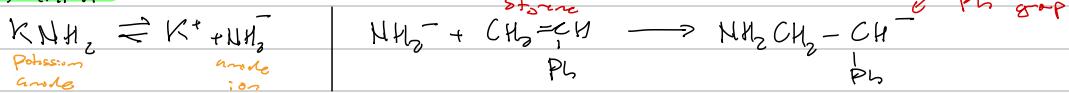


or



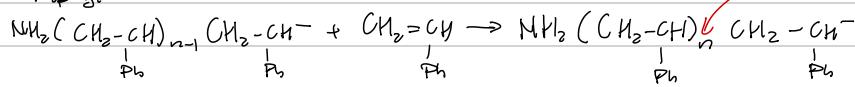
Anionic Polymerization

(i) Initiators



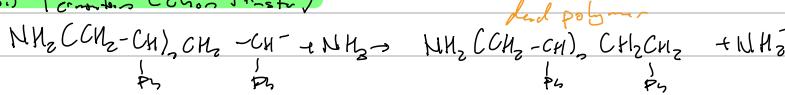
Delocalized around Ph group

(ii) Propagation



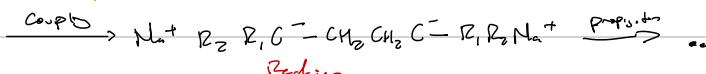
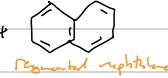
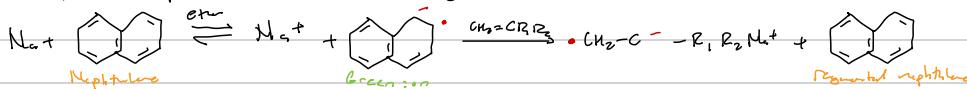
one more repeatunit

(iii) Termination (Chain transfer)



dead polymer

Example: Naphthalene as a Catalyst



Redox

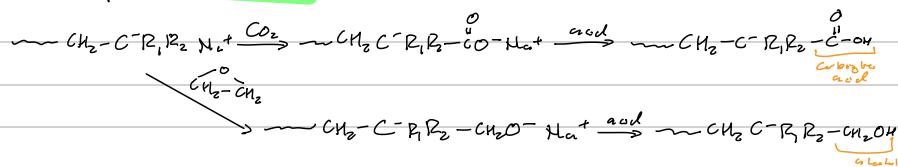
transfers

Tailored End Groups

(i) Hydrophobic Terminal Groups



(ii) Hydrophilic Terminal Groups



Summary

(i) S.Rc runs at molecular level

(ii) Sub-zero temperatures are often necessary for low molecular weight polymers

(iii) If water is present, it must be by stoichiometric ratio

(iv) H₂O is a good charge transfer agent

(v) Polymer chain purifies (glassy and melted)

(vi) Rapid complete conversion in seconds

(vii) Problem: heat loss → non-stoich. etc conditions

(viii) Only commercially Note worthy example: Synthesis of butyl rubber by copolymerization of isobutylene

• Low polymerization is faster than free radical polymerization (growing)

→ $[M^+] = \text{Concentration of propagating chain} \approx \text{Problem: Heat Transfer, non-stoich. state}$
 $\Rightarrow [M^+], [M^-] = 10^4 - 10^6 [M_0]$

• Counter ion of opposite charge

→ Degree of association influences rate and stereochemistry of propagation → polar solvents ability to solvate counterion controls

• Termination cannot occur between two growing chains (coupling)

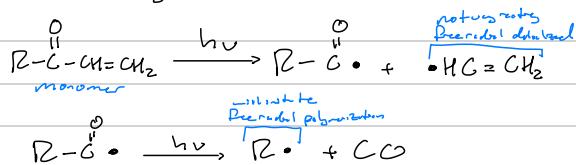
→ Active centres are of the same charge and the same charge repel each other so coupling cannot take place

⇒ Living polymerization at cryogenic temperatures

Polymerization by Other Radiation Sources

Photopolymerization

Photo cleavage of Monomer



The number of photo-cleavable monomers are limited because of the lack of ideal UV absorption for photo-cleavage. Needs to be specific monomers must absorb the light.

\Rightarrow Use a photoinitiator: Those monomers that do not have UV cleavage properties can also be polymerized.

\hookrightarrow Needs monomer or photoinitiator to be more efficient at absorbing energy

\hookrightarrow There are many photosensitizers available depends on the monomer to be used

- Using a lamp to emit UV light but some less miscible monomers can be initiated for photopolymerization or photo-crosslinking

Advantages

- (i) No contaminant by the initiator (in case photoinitiator is not added)
- (ii) Polymerization can be fast in a matter of seconds
- (iii) Photographic imaging technique (photolithography) can be used

Disadvantages

- (i) The shallow penetration depth of UV light \rightarrow cannot bulk
- (ii) Visible light can penetrate deeper and thus able to polymerize thicker films although handling of visible photoinitiator system is awkward as it must be in a dark room

Solid State Polymerization by UV

Advantages

- (i) High molecular alignment
- (ii) No initiator needed

Electrochemical Polymerization

Advantages

- (i) No pinhole free thin film \Rightarrow Corrosion Protection
- (ii) No initiator needed

Other Sources

- (i) Photopolymerization (UV or visible light)
- (ii) Solid-state photopolymerization by UV
- (iii) Electrochemical Polymerization
- (iv) Mechanical Polymerization

\rightarrow Mechanical grinding

\rightarrow Ultrasonic

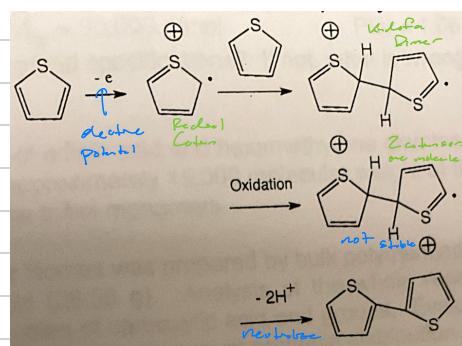
\rightarrow Microwaves

(v) Radiation Polymerization (γ -ray)

(vi) Electron beam polymerization

(vii) Thermal Polymerization

Electrochemical Polymerization Example



Final new Course in SP2S (P)

- Polymer characterization
 - \hookrightarrow Analysis and identification of polymers & polymer materials
- Types of characterizations
 - Molecular
 - Behavioral
 - Thermal
 - Mechanical

Review Lecture

Photopolymers

- As long as you are generating radicals, it follows free radical polymerization. G will increase with prop, term
 - Can follow different reaction mechanisms
 - Solid-state can also be free radical
 ↳ neither are guaranteed to follow free radical mechanism

Solid State Polymerization

↳ Start with a solid and end with a solid

Retardas & Inhibidores

Chapter 5



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 tens 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 yellow Consolidated Mixture!
- C. Sugar/water mixture X Sugar dissolves water → no heterogeneity
- D. Cotton fiber consolidated by phenolic resin yellow Materials heterogeneous & consolidated
- E. Phase-separated diblock copolymer X it depends on choice of comonomers
- F. Tire made of carbon black and polybutadiene yellow 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: C₆₀, carbon nanotube, graphene, MXENE

Functional Nano fibers: Fe₂O₃, TiO₂, 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 Plates

(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

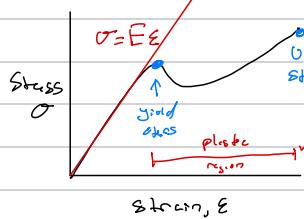
Impact Strength
tensile strength inversely proportional

Typical Measured & Test Properties Measurements

Mechanical:	Tensile Compression	Tensile Coefficient of Thermal Expansion	Thermomechanical	Dynamical mechanical
	Flexural		↔ If composite material CTE differs → breaks from shearing	↔ DMA
	Impact	HDT → Heat Distortion Temp		

Universal Testing Device & Location

Uniaxial tensile test



Arcu curve

E = Modulus of Elasticity = Young's Modulus

Sometimes use 3-point bending test

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

↳ Charpy Impact Tester used as well

Adding Calcium
Carbonate 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 ($\frac{E_{\text{Pc}}}{\text{density}}$) $E \frac{\text{GPa}}{\text{cm}^3}$

- 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 (PIZO): ↓ 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:

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

σ_{fu} : fiber tensile strength σ_m : stress carried by the matrix Q fiber fraction
 V_f : fiber volume fraction V_m : matrix volume fraction

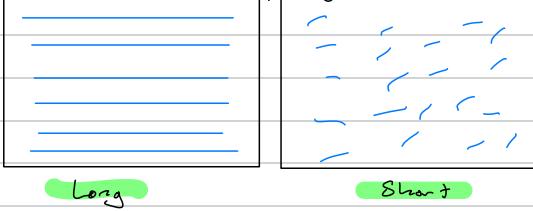
Short Fiber composite fail catastrophically - used for everyday use

- Different fibers/matrix should be used for different applications

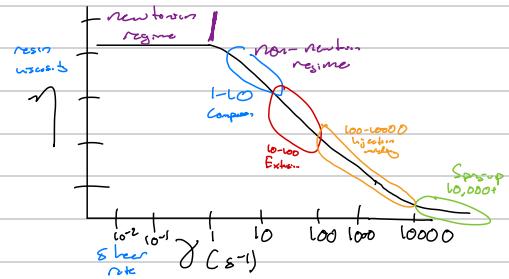
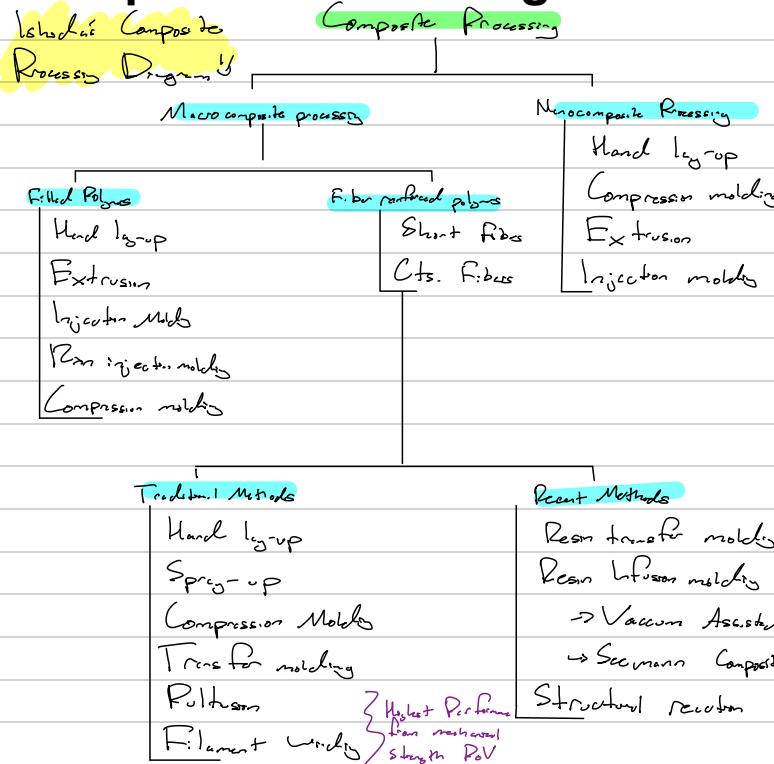
Long vs. Short Fiber reinforcement

• 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



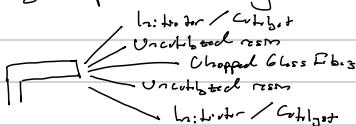
Hand Lay-up Molding

- 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 sheet. 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

- E.g. Spraying is much lower as grinds not mix resin with initiator
- **Room Temperature Curing**
 - \rightarrow Much cheaper than buying a large furnace
 - \rightarrow Time constraints are to issue
- **Advantages:**
 - i) Mold \rightarrow Small Particle Size
 - ii) Leads to \uparrow up pressure
 - iii) Highly versatile and designs are flexible
 - iv) 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
 - v) Low productivity

Carbon: Cuts trapdoor failure of trap door is possible

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
- **Operation:** 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

☒ (iv) Most versatile method Geometrically different shapes we have access to

(ii) Some labor is needed to clean the flash

(iii) Energy intensive

↳ 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 \rightarrow 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 \leftarrow 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

\bullet 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

(ii) The only truly cont. process for

cts. fiber reinforced polymer

\hookrightarrow Not true for batch operation, only limited for continuous ones

\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

(i) Could use a plastic 'billet' as a mandrel, composite acts as support \hookrightarrow **Example:** Massive Fuel Tank for Saturn rocket used for the upper stages, Pressure tanks, Golf Club shaft, Rotor blade

Hobbyist Put

(ii) Remove Mandrel from small openings \hookrightarrow Make mandrel out of plastic which dissolves under high pressure heat water

Mandrel is put up to golf club

(iii) Dissolve Mandrel into resin to remove the mandrel

Advantages: (i) Strongest composite of all

Disadvantages:

(i) Low productivity and expensive

processing methods

\hookrightarrow costs are high & very time consuming

(ii) Does not require constant cross-sectional area

Advantage: (ii) of Polymers still holds as this is a batch process, polymer does not change

\hookrightarrow This is a High Performance Technique

it can be continuous

Final Exam



Goal: Homogeneously Review Semester's Topics

Final Exam Tips & Suggestions

- About 50 questions - can finish in 30 minutes, but you can take your time
 ↳ 5 choices per question (entire exam is multiple choice)
- Homogeneous examinations of all students for topics
- Don't overcheck your work → allows doubt to creep in
- No calculator required, can all be done in your head if absolutely necessary
- Superficial content, not analytical
- TA review sessions, included in a future email blast
- 30 pts extra credit to whole class if $F \geq 90\%$. Do course evaluations

Final Exam In Class Review

Processing

Want to make an arrow for archery. What processing method do you suggest?

Pultrusion - same diameter throughout, needs to be strong!

Processing method to make rocket cases of 2m diameter?

Filament Winding, can use hand lay up, but you want the highest possible winding

Zinc Oxide ABS Polymers?

Injection Molding - small intricate object needs to be produced

Use of Continuous Fibers (some, not all)

Pultrusion, Filament Winding, Hand Layup, Resin Transfer

Confinement

1-D: Between plates

2-D: In a tube

3-D: In a sphere

Chain Transfer

In transition state, but doesn't result in a chain free

Radical concentration

Polymers vs. Metals & Ceramics

Metals: No covalent bonds, atoms interact purely \rightarrow strong and high moduli

Ceramics: Similar to metals

Polymers: Covalent bonding and Van der Waals present which makes weaker than atomic forces

Lattice Theory Problems

Assumes: Space occupied by solvent or CRU are equal in size

- Assumptions ok at first glance, but there are issues in real applications

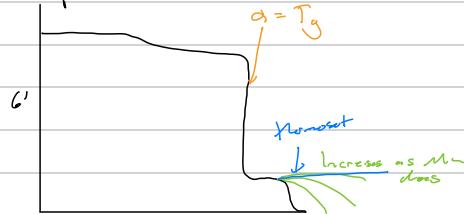
channel repeat unit

DMA

Run DMA of unknown polymer. It was relatively steady G', then saw a drop into a plateau. After a bit of plateau, it dropped off a bit. I then concluded that the polymer was a unique thermoset polymer.

\Rightarrow False - Polymer flows so it is a thermo plastic!

Spectrum



Marmott Model

Used for Stress Relaxation Phenomenon

Free radical is short but will be very

Polymerization for Block & Graft

Living Polymerization best for Block Copolymer

Characterization

Want to use C-13 to study main chains of polymer, but 13C NMR technique is useless to determine structure due to similarity of two molecules linear frequencies.

False - Linear frequency of C-13 is constant, but surrounding environment of molecule is different, thus is the chemical shift concept.

Want Scattering Method for MW... Absolute or Relative?

Absolute Chromatography is relative and most common, but colligative properties are absolute

Injection Molding

→ Reinforced: Short Fibers

→ Structural: Larger fibers in preform put into amorphous moldings

Autoacceleration

Happens because polymerization influences viscosity → lesser polar Free radicals react more → Free radical concentration changes and stop coupling → steady state violated