

Term Paper Introduction

General Notes

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- (i) Do not cite web addresses as references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

Possible Term Paper Subjects

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

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

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

ASK Questions!

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

Chapter 1



Goal: Refresh information from ENGR145

Concepts and Nomenclature

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

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

Macromolecules: Contain both polymeric and non-polymeric large molecules

How many units to be polymers?

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

Not repeating

00 "

0△0 "

0△△0 Beginning of structure

Structure of Polymer Chains



Copolymers

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

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

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

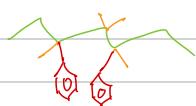
Conformation vs. Configuration

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

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

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

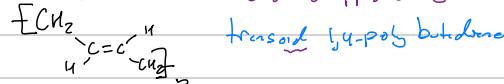
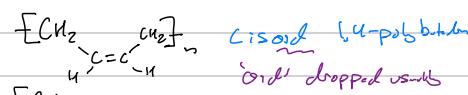
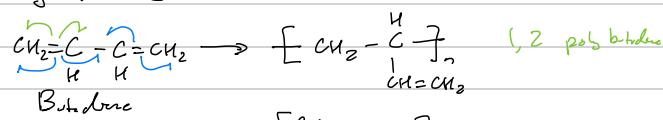
Can crystallize
↳ Material looks shiny

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

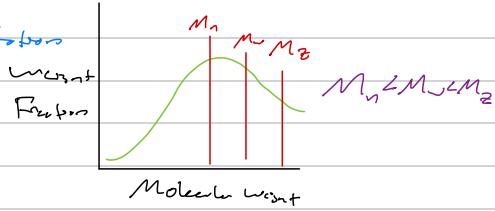
$$\text{Weight Avg MW: } M_w = \frac{\sum W_x M_x}{\sum W_x} \quad \text{How, } W_x = N_x M_x \rightarrow M_w = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

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	$10^3 - 10^5$
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

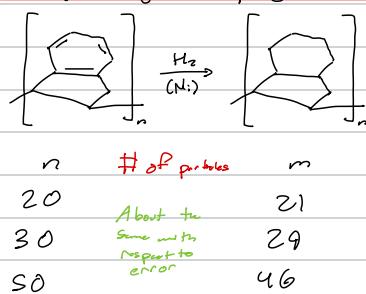
Meas Method: Colligative property Measurement



Discussed Degree Polymerization as the method was aggregate of molecules

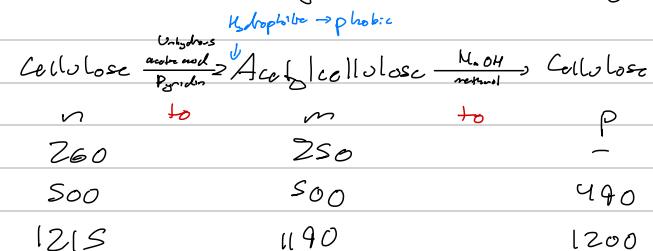
Staudinger's Experiments

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

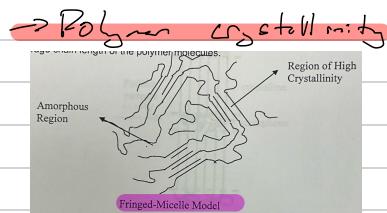
Critics stuck as they rebutted all they were arguing
Covalent Bonds provide as structure constancy

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

Viscosity is more sensitive to larger MW molecules than smaller ones

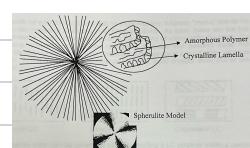
Morphology

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



\rightarrow Spherulites

Polarized light reveals a molten cross (X)

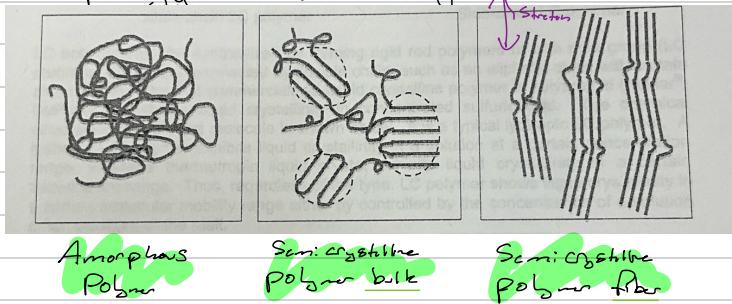


\rightarrow Lamella Structure

Adjacent rotary model
 \rightarrow thought to occur due to energy preference

Today Adjacent is a more favorable explanation

Morphology Control: Stretching

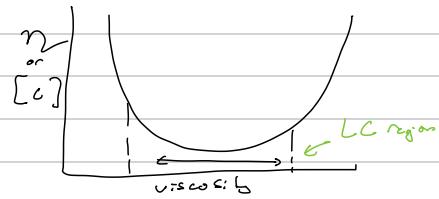


Stretching

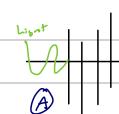
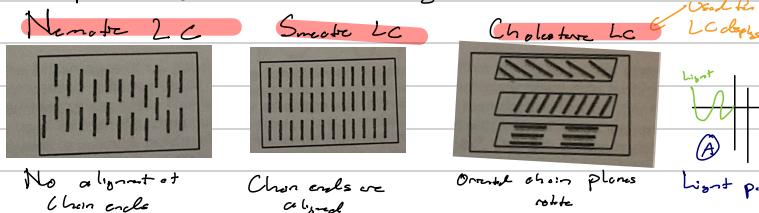
- Molecules realign along stretching direction.
- \uparrow stretching \rightarrow \downarrow intermolecular distance
 - \rightarrow leads to crystalline region formation
- Cracks are also observed along stretching direction
 - \rightarrow Thus the fibers or structural films are stronger along stretching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

Liquid Crystalline (LC) Polymers

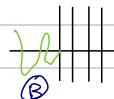
liquid = amorphous
crystal = perfectly ordered } Two opposing words used to express unusual material
that is neither completely amorphous nor ordered



Types of LC Polymers



vs.



Light passes through ① as it needs transverse alignment

Allows microwaveable

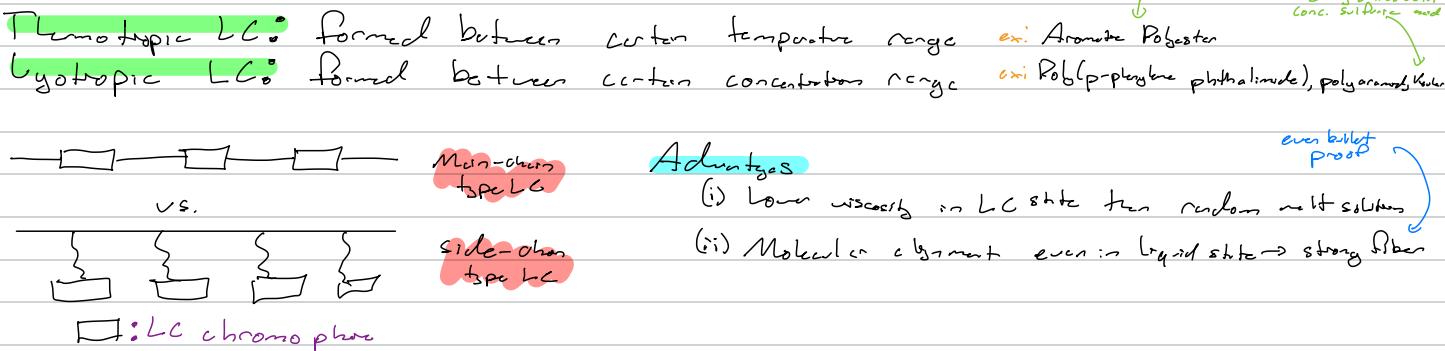
Supperware

only dissolving conc. sulfuric acid

Sustaining orientation
the longer so lighter
rotate up and out

Cholesteric LC: formed between certain temperature range ex: Aromatic Polyester

Lyotropic LC: formed between certain concentration range ex: Poly(p-phenylene phthalimide), polyaramid Kevlar



Advantages

- (i) Lower viscosity in LC state than random melt/solvent
- (ii) Molecular alignment even in liquid state → 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!

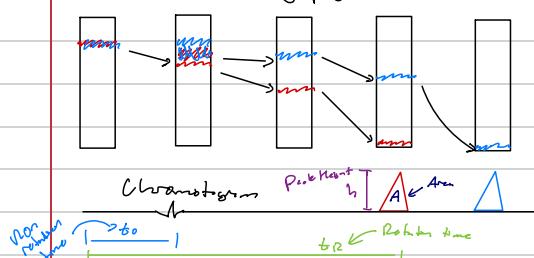
(ii) SEC (Size-Exclusion Chrom)

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

Cannot use on solids which don't dissolve or evaporate

Gradient Systems

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

Typical one used

Reversed Phase Chromatography

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

Hydrophobic → Hydrophobic surface charge

en: Phenols are hydrophobic

so it avoids hydrophobic surfaces.

Untreated silica gel is usually used (Acidic)

Acid/Base interactions > H-bonding ones

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

Sizing Exclusion Chromatography

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

Think of it like trying to explore a tight cage

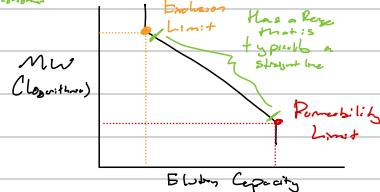
- Huge molecules come out first as small ones need to go through a lot of pores
- Uses cross-linked polystyrene → Created with vinyl aromatic monomers
↳ This means most polymers will interact with the substrate

Separation Principle

→ Molecules $>$ Pore size cannot enter!

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

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



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

Infrared Spectroscopy

Photon in → Photon out

↳ Invisible radiation outside of the red

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

Detects Vibrational Motion

Uses of Vibrational Spec

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

Advantages

- Sensitive, Rapid
- Spectra easy to see

Disadvantages

- Chemical process
- Hard to interpret.

Spectral Analysis

A spectrum completely defined when following spectral parameters are specified

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

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

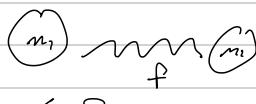
Model For Vibrational Spectroscopy

↳ Point masses bonded with a Hookean Spring

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



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



Hookean spring
resting force: f

← Displacement → (z)

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

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

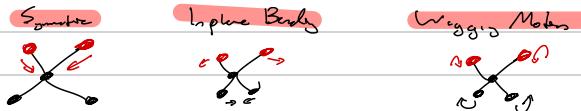
Frequency



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

• Frequency Higher with smaller masses!

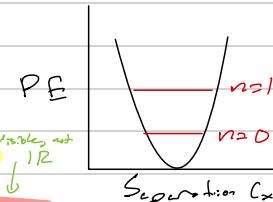
Analysis of Methylene Models



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
- Charges in permanent dipole moment upon vibration

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

(ii) Raman

Characteristic Group Frequencies

Use characteristic Frequency table to determine groups!

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

Molecular 1D-Basis

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

CWIR Evolution

- Albert Michelson: Michelson & Morley → Nobel Prize

↳ Prof. of Physics at Cesc

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

- Jack Koening: First Raman study of carbon

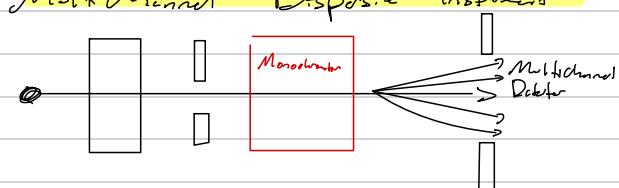
- H. Ishida: FT-IR analysis. Optical Techniques

Dispersive Infrared Instrument



Solution

Multichannel Dispersive Instrument

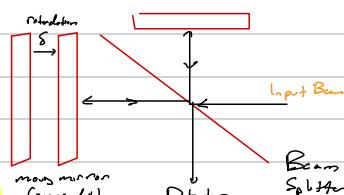


Disadvantages

- 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

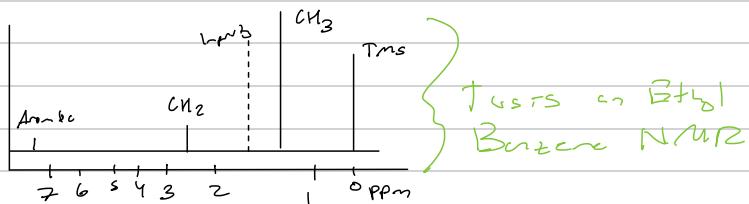
Disadvantages

- 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

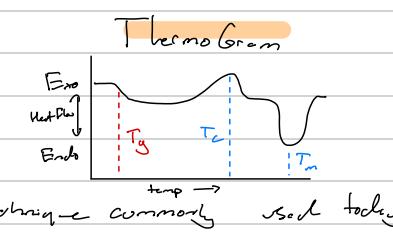
→ Small Endo peak may appear due to shippers / purity issues

- 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



Enthalpy relaxation
phenomenon



Reversing and Non-Reversing Contributions to Total DSC Heat Flow

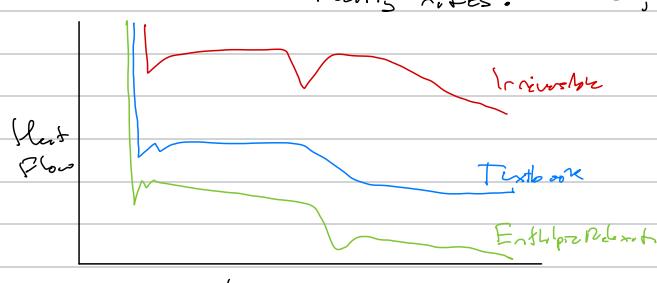
$$\text{Total Heat Flow} \rightarrow \frac{dQ}{dt} = C_p \cdot \frac{dT}{dt} + f(t, T)$$

Non-reversible heat component
Reversible signal

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

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

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

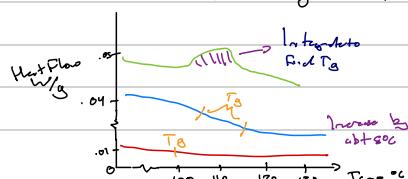


Reversible vs. Non-Reversible Transitions

Reversible: Glass Transition, melting

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

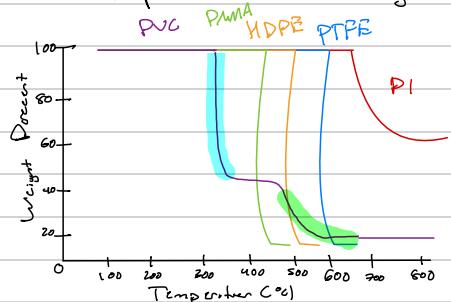
TMDSC Thermograms for Nanocomposites with 50 wt% of Polystyrene



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

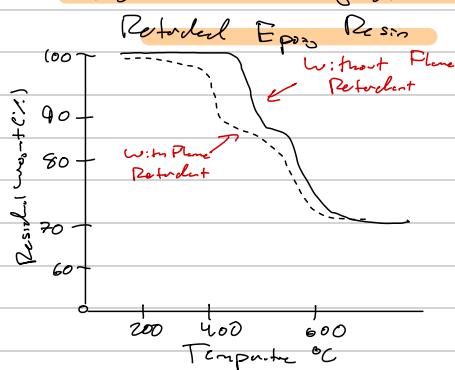


What's going on with PVC?

• 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
 ↳ Gives an Activation Energy Spectrum!

Activation Energy

Good Journals don't

Accept single analytical result

TGA-based hyphenated techniques

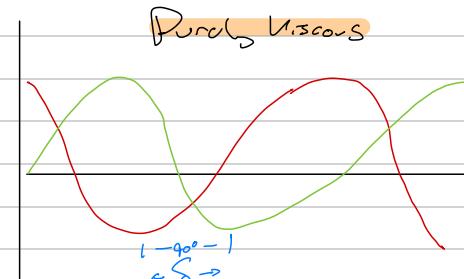
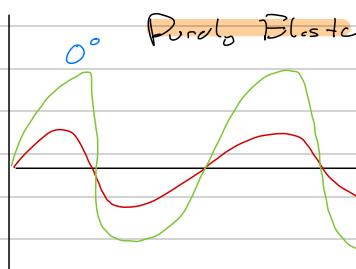
- TGA measures weight quantitatively
- TGA allows controlled decomposition
- Evolved gases are difficult to separate
- Reactor analysis of evolved gas minimizes secondary structure formation
- **DSC-TGA:** Measures both heat flow & weight changes as a function of temp or time
 ↳ Simultaneous DSC-TGA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

melt & crystallization

Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA)

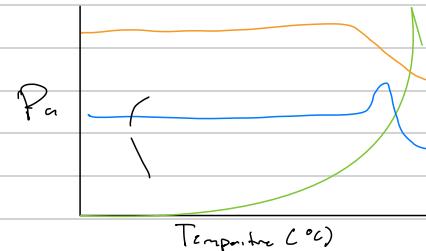
- Sample moves in sinusoidal motion instead of static/stress techniques
 - ↳ Bottom line: static stress actually changes the polymer structure
- Sinusoidal stress on a sample applied to measure stress in terms of phase lag
- You can learn:
 - (i) G' : storage modulus (recoverable energy)
 - G'' peak is $T_g \rightarrow$ (ii) G'' : loss modulus (irrecoverable energy lost as heat)
 - (iii) 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 measurements.

Polymer DMA Spectra

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



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

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

Use non-crossing based analysis for more rigorous study
 ↴
 Gelation occurs when G_1 and G'' cross (not fully accross but used for convenience)

Chapter 3



Goal: Study polymer & composite processing techniques

Composites & Nanomaterials

Composite

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

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

- Exhibit properties of its component materials

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

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

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

- Classifications of Composites

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

↳ Poor fiber/matrix interface can initiate cracks

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

↳ Small amount of reinforcement exhibits significant prop. improvement

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

Other Jargon

→ Reinforced Polymers - Composites w/ Fibrous materials

→ Filled polymers - polymers w/ particulate fillers

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

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

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

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

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

→ Fillers - Materials other than continuous fibers

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

→ Roving - Many sets of strands are bundled together

Which ones are composites?

yellow = yes; blue = sometimes

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

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

Raw Materials for Composite Manufacturing: Reinforcements & Fibers

(i) Fibers

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

(ii) Fibers ← Reinforcement to be bonded

Ordinary portlandite fibers: Silica, wollastonite, calcium carbonate

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

Nano fibers: 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 Fibers

(i) Thermosetting Resins

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

(ii) Thermo plastic Resins

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

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

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

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

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

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

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

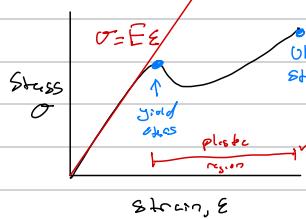
Impact Strength
tensile strength inversely proportional

Typical Measured & Tested Property Measurements

Mechanical:	Tensile 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



Ultimate Strength

Curve

Impact E

$E = \text{Modulus of Elasticity} = \text{Young's Modulus}$

Sometimes use 3-point bending test

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

↳ Charpy Impact Tester used as well

Adding Calcium
Carbonto to PE
causes tensile strength
to decrease.

Addition of Fillers

Example: Billiard Balls

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

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

- 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:

$$\sigma_{in} = \sigma_{f_u} V_f + \sigma_{m} V_m \quad (1)$$

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

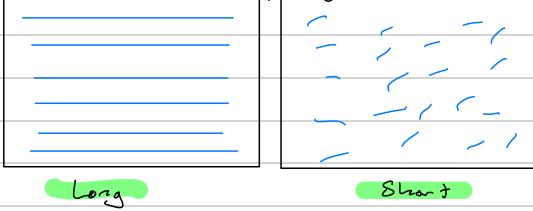
Short Fiber composite fail catastrophically - used for everyday use

- Different fibers/matrix should be used for different applications

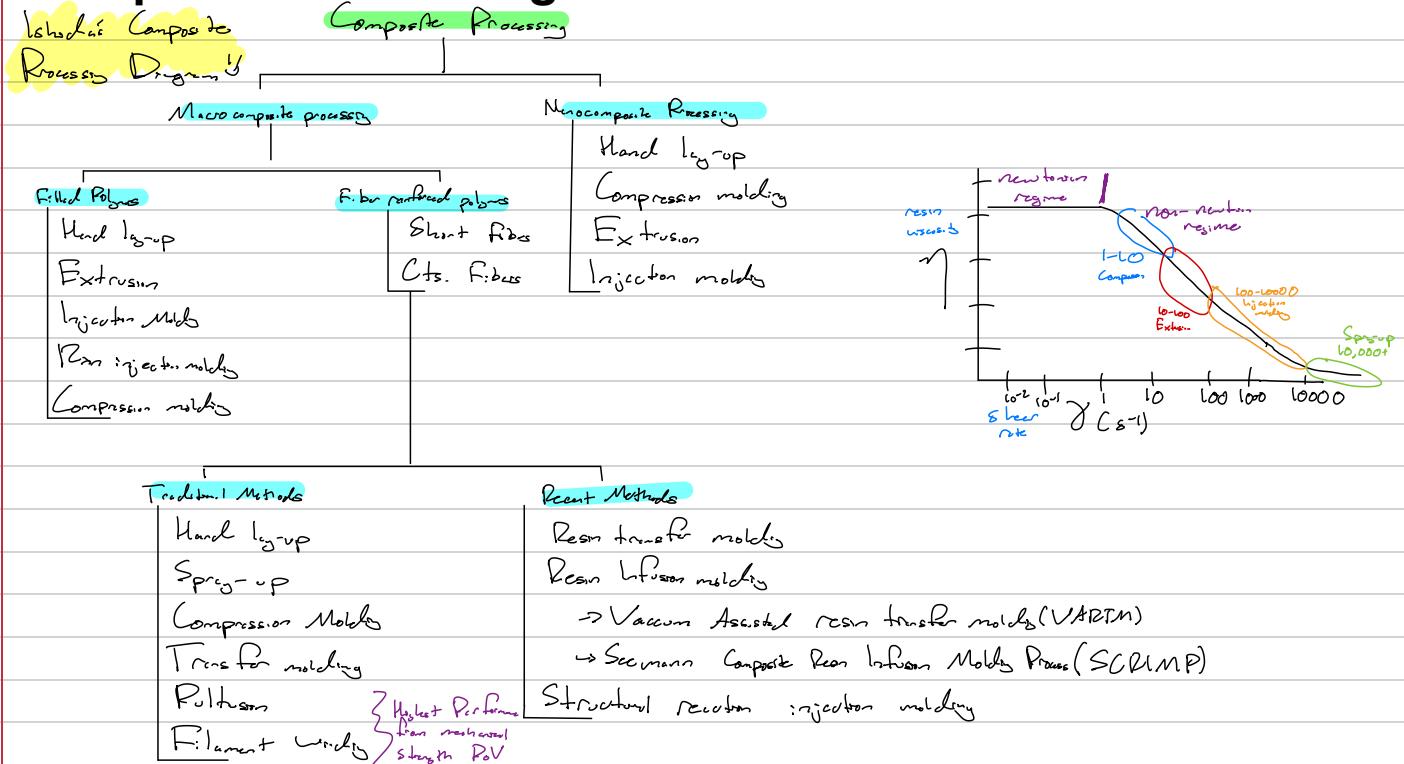
Long vs. Short Fiber reinforcement

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

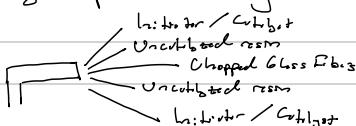
- Cracks will only propagate if it exceeds its Griffith crack



Composite Processing



Spray-up Molding



Note: Catalyst is not forced to mix with resin → material intensive

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

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

Advantages: (i) Cost is much lower as grinds not mix resin with initiator
↳ Room Temperature Curing

→ Much cheaper than buying a large furnace

→ Time constraints are less

Advantages: (i) Mold → Small Partole Size
↳ Leads to ↑ vapor pressure
Needs fire Dept Approval → a carcinogen

(ii) Handling versatile and designs are flexible

(iii) 2-3 times improved productivity to hand lay-up

(iv) Environmental concerns
↳ Added expenses

(v) Still labor intensive
↳ Still high Setup rate

(vi) Low productivity

Caution: Cuts trapdoor failure of trap door is possible.

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

Everything up to

Basic Compression molding (not include advanced)

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 over wide part which is labor intensive remove/cut (Called trim flash)
- Most versatile out of transfer 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)
- (ii) Mid-Rate Productivity (composites)
- (iii) Not too labor intensive
- (iv) Most versatile method Geometrically complex shapes we have access to! Form OB sizes/labor intensive

Disadvantages

- (i) In-trim shaped objects cannot be molded
- (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
- Material is not placed in mold cavity!- ↳ Transfer into cavity by using hydraulic pressure
- Easy to cut flash

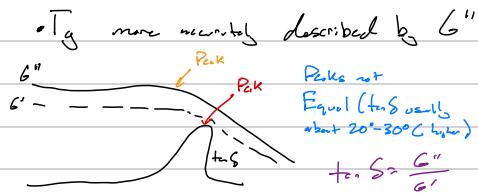
Midterm Review

- $\geq \frac{1}{2}$ Quatitative
- $\leq \frac{1}{2}$ Quantitative Like MW calculations

Can use images/graphs on term paper but must cite!

Can send email Questions, lab will respond up until 6pm Sunday

DMA



TG/TGA Techniques

- Using Thermal Probes, you study thermal Probs
- Ex: DMA measures T_g
- DSC uses therm to get therm.

Review Monomers, Polar structures, and thermoplastics/thermoset properties

Agree or Disagree

I observed amorphous polystyrene cup dropped into candle making fireball as it drops onto Flame Therefore I will not use it for fire safety techniques. **I Disagree, Amorphous materials should not melt!**

Main Chain LC vs. Side Chain LC

- Main Chain - between mech prop like LC due to polarity
- Side Chain - somewhere between main chain LC and non-LC polymers

Techniques

• Standard b/c able to : dnt & techniques to be used given a set of desired materials/efficiencies

Composite

- May different ways to make composites thermal and electrical properties
- How they impact electrical Properties
- Carbon Black can be added to PE \rightarrow Carbon Black is conductor but as more heat up, carbon black separates \rightarrow insulating

NMR Should also know the fundamentals of each technique

- Larmor Frequency for one proton is same under a specific magnet
 \hookrightarrow can determine chemical environment with Larmor Frequency as number bond around molecule changes its magnetic field

Extrusion for Composites

- Calcium Carbonate
- Wood Powder

Hand Lay-Up & compression molding

- They cube strong : ftg usc strong pts. filament
- Spry-up can't use pts. filament \rightarrow not as strong

Strong meaning better mechanical properties

Composite vs. Non-Composite Examples

(1)

How do we know type of Crystalline LC

- Morphology! Use instruments to observe
- Melting Cross Secn in microscope \rightarrow spherulite
- Fiber with mutual surrounds + tangent \rightarrow trans crystals
- See various types of cross sections \rightarrow different type of crystal