EMA5646
Ceramic Processing
4 Processing Additives

FLORIDA INTERNATIONAL UNIVERSITY

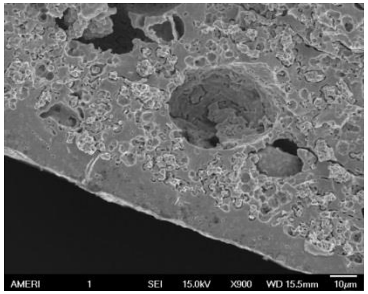
Additives in Ceramics Processing

❑ Additives are added in ceramic processing

- Control feed materials characteristics
  - Example: Flow capability
- Achieve designed shape
  - Examples: tape, cast green body, extruded form…
- Control packing of the green body before firing
  - Porosity/relative density
  - Uniformity

Difference in flow capability
http://www.aerosil.com/product/aerosil/en/industries/pharmaceuticals/solid-drug-forms/Pages/default.aspx

Slip-casted clay pot
https://britehub.com/manufacturing/casting/slip-casting



NiO-YSZ/YSZ bilayer co-sintered
Cross-section
SEM by Shichen Sun

❑ Features

- Except for solvents, additives are added at low percentage level (by weight) or even lower
- Most additives are organics that later get removed in subsequent firing (sintering)
- Inorganic additives leave residual and are used mostly for traditional ceramics where small composition variation is not too critical

Reed (1995), p. 135
Rahaman (2003), p. 344

Common Types of Processing Additives

- **Solvents/dispersion medium**
- **Dispersants**

  Agents to help disperse ceramic powder in solvents and help stabilize slurry against flocculation and/or sedimentation
- **Binders**

  Agents to help glue/bind particles and increase strength of green body. In some cases, also include flocculants, which cause particles to floc in liquid suspension
- **Plasticizers**

  Agents to help increase plasticity of green body
- **Other**
  - Foaming agent – agent to help foams formation
  - Antifoaming agent - agent to defoam or repress foaming
  - Lubricant – agent to lubricate between tool surface and ceramic green body
  - Wetting agents
  - Bactericide/fungicide – agent to kill bacteria/fungus

Reed (1995), p. 135

Rahaman (2003), p. 344

Solvents & Water as a Solvent

❑Solvents

Additives to provide a (viscous) medium between particles to enable fluidity and also to dissolve additional additives in order to achieve certain mechanical, especially rheological behavior and disperse particles and additives uniformly

❑Water

- Low cost, safe, environmentally friendly $\rightarrow$ used in most cases
- Good solvents for polar and ionic compounds
- Boiling point of 100 ^{o}C and melting point of 0 ^{o}C; High surface tension (73 mN/m) and dielectric constant (80), low viscosity (~1 mPa • s)
- pH 7 when neutral
- When highly pure, conductivity of 0.055 μΩ/cm (resistivity 18×10^{6} Ω • cm) at 20 ^{o}C
- "Hardness" – due to dissolved Ca, Mg, and other salts.
  Total dissolved solids (TDS) can be estimated from measured conductivity C (in unit of μΩ/cm) via

$$TDS(ppm) = \frac{C(\mu\Omega / cm) - 0.055}{2.5}$$

- Filtration and/or ion exchange could purify water TDS to low ppm level
- Recycled when possible (e.g., grinding/polishing, washing)

Reed (1995), p. 137-142

Rahaman (2003), p. 345-347

Organic Solvents

❑Disadvantages compared with water

- Flammable and even explosive
- Volatile and giving vapor that not only odorous and, in many cases, hazardous
- May be toxic and difficult to dispose
- Expensive

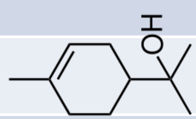
Ethanol (C_2H_5OH)

❑Use

- If water reactive (e.g., $BaTiO_3$, AlN, or Si_3N_4) or sensitive (e.g., LIB battery electrode)
- To achieve very high solid loading (e.g., >80 wt%)
- For special applications that
  - Require higher boiling point (e.g., screen printing using terpineol)
  - Require better wetting (e.g., thin film formation and printing using terpineol)
  - Require faster drying (e.g., tape casting using toluene or MEK) or higher evaporation rate
  - Avoid contamination and/or electrical shorting
- Industrial trend - **<u>gradual shift to more water based systems</u>**
  - Examples: paint, LIB electrode processing

Reed (1995), p. 137-142
Rahaman (2003), p. 345-347

Properties of Some Common Solvents

	Formula	Dielectric constant	Surface tension (mN/m)	Viscosity at 20 °C (mPa s)	Boiling point (°C)	Flash point (°C)
Water	H_2O	80	73	1.0	100	None
Methanol	CH_3OH	33	23	0.6	65	18
Ethanol	C_2H_5OH	24	23	1.2	79	8
Isopropanol	C_3H_7OH	20	22	2.4	83	12
n-butanol	$CH_3(CH_2)_3OH$	18	25	2.9	118	35
Ethylene glycol	$HOCH_2CH_2OH$	37	48	16	197	111
Glycerol	$HOCH_2CHOHCH_2OH$	43	48	20	290	160
Acetone	CH_3COCH_3		22	0.3	56	-20
Methyl ethyl ketone (MEK)	$CH_3COCH_2CH_3$	18	25	0.4	80	-9
Terpineol	$C_{10}H_{18}O$ 		33	61	217	95
Trichloroethylene	$CHCl=CCl_2$	3		5.5	87	

Dispersants

❑Application

Additives to help disperse ceramic particles (as well as other phases) in solvents and stabilize slurry (particle suspension) against flocculation (formation of soft agglomerates from finer particles) and/or sedimentation

❑Mechanism of stabilization

- Electrostatic

  Lead to repulsive force between particles of similarly charged surface

- Steric

  Lead to repulsive force between adsorbed polymer molecules over particles

- Electrosteric

  Combined electrostatic and steric actions

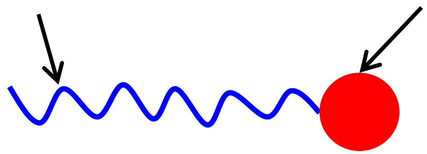
❑Types of dispersants

- Short-chain polymers with a functional head group or **surfactants**
- Low to medium molecular weight **polymers**
- **Simple ions and molecules**

Surfactants as Dispersants

❑Surfactants

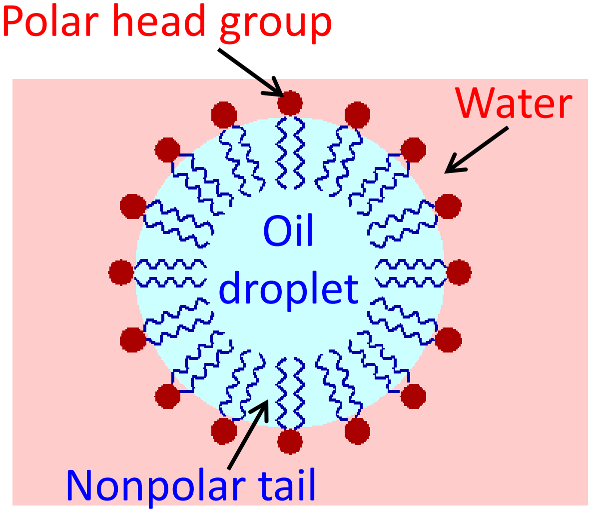
Molecules of special design that have one **polar head group** and a **nonpolar organic tail** that help dispersion of one phase (solid or liquid) in another liquid phase



❑Nonpolar tail and polar head group

- Nonpolar (hydrophobic/lyophobic/lipophilic) tail
  - Short chain organic tail (MW < ~50-100) that repels water or other polar substance surface while attracting non-polar molecules, e.g., vinyl $-(CH_2)_n-$
- Polar (hydrophilic/lyophilic/lipophobic) head group
  - Attracts water or other polar solvents or surfaces while repels non-polar solvents or surfaces e.g., hydroxyl (-OH), carboxyl (-COOH), sulfonate ($-SO_3^-$), sulfate ($-OSO_3^-$), ammonium ($-NH_4^+$), amino ($-NH_2$)

Fine dispersion (emulsion) of oil in water (or micelle)



https://en.wikipedia.org/wiki/Surfactant

❑Surfactant features

- Added at very low level such as 0.01-0.1 wt% with respect to the dispersed phase
- Reduces surface tension/interfacial energy

Classification of Surfactants

❑Nonionic surfactant

Do not ionize (form charged ions) in solvents

❑Anionic surfactant

Has relatively large negatively charged polar (hydrophilic) head group and large non-polar (hydrophobic) tail

- Widely used
- Tends to adsorb on surface neutral and positive particles

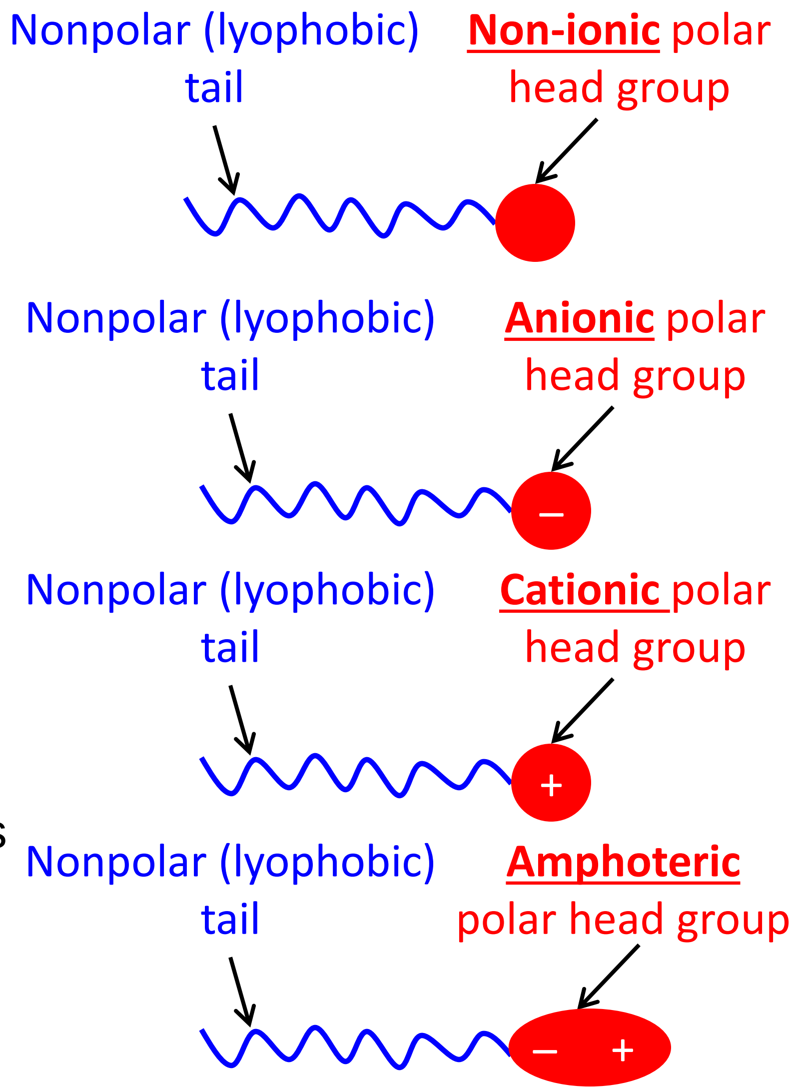
❑Cationic surfactant

Has relatively large positively charged polar group and large non-polar tail

- Tends to adsorb on surface negative particles

❑Amphoteric surfactant

Has both cationic and anionic center attached to the same molecule and can be anionic or cationic depending on pH



Examples of Surfactants & Effects on Surface Tension

SODIUM DODECYL SULFATE
(SODIUM LAURYL SULFATE)
IONIC SURFACTANT

$$\underbrace{CH_3-(CH_2)_{11}}_{\text{Hydrophobic}}-\underbrace{O-SO_3^-\ Na^+}_{\text{Hydrophilic}}$$

(OCTYLPHENOXYPOLYETHOXYETHANOL)
NON-IONIC SURFACTANT

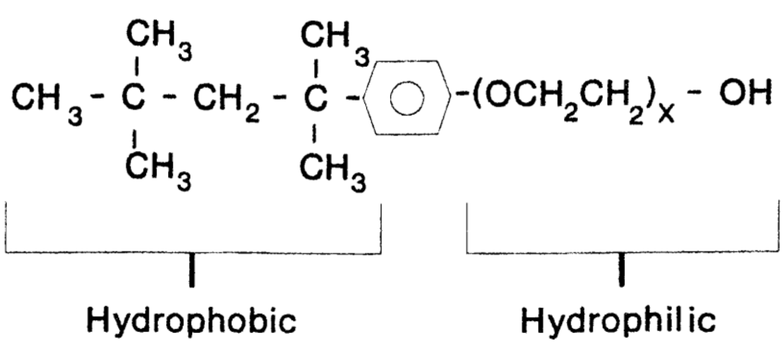
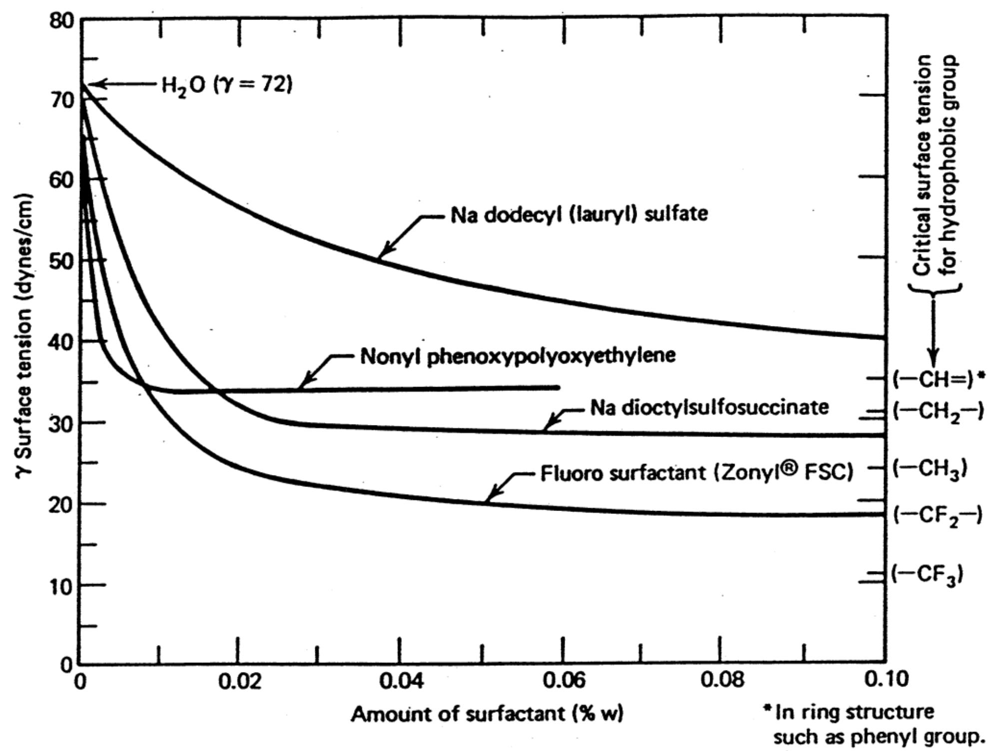


TABLE 9.4 Examples of Surfactants

Type	Generic Name	Composition
Nonionic	Ethoxylated nonylphenol	$C_9H_{19}(C_6H_4)O(CH_2CH_2O)_{10}H$
	Ethoxylated tridecyl alcohol	$C_{13}H_{27}O(CH_2CH_2O)_{12}H$
Anionic	Sodium stearate	$C_{17}H_{35}COO^-Na^+$
	Sodium disopropylnaphtalene sulfonate	$(C_3H_7)_2C_{10}H_5SO_3^-Na^+$
Cationic	Dodecyltrimethylammonium chloride	$[C_{12}H_{25}N(CH_3)_3]^+Cl^-$



Reed (1995), p. 142-143

HLB Number for Surfactants & Suspension

❑Hydrophilic-Lipophilic-Balance (HLB) Number

- Arbitrary number to quantify the relatively strength of the polar/hydrophilic (H) and non-polar/ lipophilic (L) groups within a surfactant or solvent or solid molecule:
  0 – extremely lipophilic/non-polar/hydrophobic
  20- extremely hydrophilic/polar
- One way to get it: for a molecule, the HLB number for each group is added to give the overall HLB number
- Range of HLB for common applications

Group	HLB Number
$-SO_4^-Na^+$	39.0
$-COO^-K^+$	21.0
-COOH	2.1
-OH	1.9
-O-	1.3
$-CH_2-$	0.47
$-CH_3$	0.47

Surfactant HLB range	Application/Function
3-6	Water (dispersed phase) in oil (solvent) emulsifier
7-9	Wetting agents
8-18	Oil (dispersed phase) in water (solvent) emulsifier
13-15	Detergent
15-18	Solubilizer

Classnotes, M D Sacks

Estimation of HLB Number

❑Using water solubility to estimate HLB number

http://www.floratech.com/fileMgr/upload/files/TestMethods/TW10.pdf

Water solubility	HLB range	Examples
No dispersability in water	1-4	Triolein
Poor dispersability	3-6	
Milky dispersion after agitation	6-8	Cottonseed oil
Stable milky dispersion	8-10	Paraffin wax, mineral oil
Translucent to clear dispersion	10-13	Kerosene, silicone oil
Clear solution	13+	Stearic acid, Polysorbate

❑Additional references

- Surfactants Classified by HLB Numbers, Sigma-Aldrich

http://www.sigmaaldrich.com/materials-science/material-science-products.html?TablePage=22686648

- AkzoNobel surfactant guide

http://sc.akzonobel.com/en/fabric-cleaning/Documents/AkzoNobel_tb_HlbEmulsions.pdf

Low to Medium Molecular Weight Polymers as Dispersants

❑Description

Polymer dispersants with molecular weight of several hundred to several thousand

❑Type

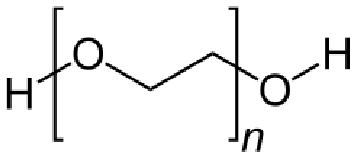
- Non-ionic
  - Polyethylene glycol (PEG)
  - Poly vinyl pyrrolidine (PVP)
  - Poly vinyl alcohol (PVA)
- Ionic (also called **polyelectrolytes**)
  - Poly methacrylic acid (PMA)
  - Poly vinylsulfonic acid
  - Polyethyleneimine (PEI)

❑Feature

- Solubility depend on chain side group: -OH or other highly polar groups dissolve in water; others in organic solvents
- Adsorb on particle surface by van der Waal’s force or coordination
- May also be used as binders in some cases

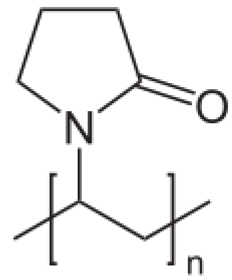
Structures for Some Polymer Dispersants

PEG



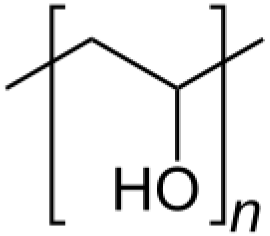
https://en.wikipedia.org/wiki/Polyethylene_glycol

PVP



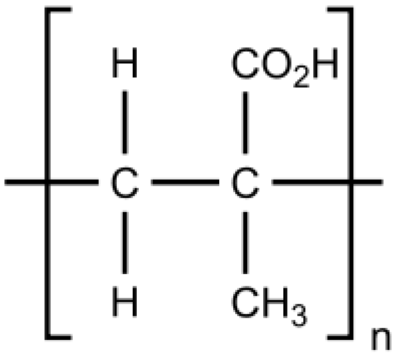
https://en.wikipedia.org/wiki/Polyvinylpyrrolidone

PVA



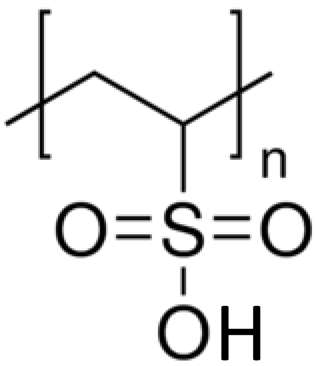
https://en.wikipedia.org/wiki/Polyvinyl_alcohol

PMAA



https://en.wikipedia.org/wiki/Poly(methacrylic_acid)

PVSA



PEI

https://en.wikipedia.org/wiki/Polyethylenimine

Simple Inorganic Ions and Molecules as Dispersants

❑For aqueous suspension

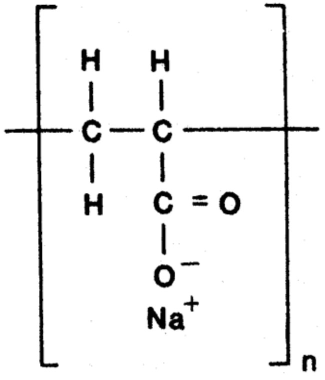
Simple ions and molecules can be effective dispersants, and the agent is sometimes also termed as **deflocculants**

❑Formation: Dissolution of electrolytes (salts, acids, or bases)

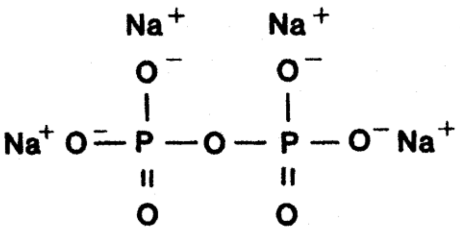
Preferred adsorption of certain ions on the ceramic particle surface coupled with formation of diffuse layer of the counter-ions leads to electrostatic stabilization

- Examples:
  - For oxides:
    - Tetrasodium pyrophospate ($Na_4P_2O_7$);
    - Sodium carbonate (Na_2CO_3)
    - HCl
  - For clays
    - Disodium silicate (Na_2SiO_3)

Reed (1995), p. 155



Sodium Polyacrylate



Sodium Pyrophosphate

Binders

❑Definition (Narrower yet common)

"help improve the strength of the as-formed product to provide strength for handling (green strength) before the product is densified by firing" (Reed (1995), 173)

❑Classification and examples

	Organic	Inorganic
Colloidal	Microcrystalline cellulose	Kaolin clay
Molecular	Natural gum (e.g., gum arabic)	Soluble silicate (e.g., $Na_2O{\bullet}(SiO_2)_n$)
	Polymerized alcohols (e.g., polyvinyl alcohol PVA)	Organic silicate (e.g., $Si(OC_2H_5)_4$)
	Polymerized butyral (e.g., polyvinyl butyral or PVB)	Soluble phosphates (e.g., Na_3PO_4)
	Cellulose ethers (e.g., ethyl cellulose EC)	Sodium aluminate (e.g., $Na_2O{\bullet}Al_2O_3$)
	Polysaccharides (e.g., refined starch)	
	Polymerized glycol (e.g., polyethylene glycol or PEG)	

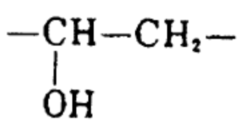
See also: http://digitalfire.com/4sight/education/binders_for_ceramic_bodies_345.html

Water Soluble Binders

- **With polar side groups:**

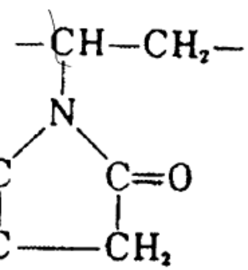
  e.g., PVA, PEG, methyl cellulose, starch

PVA



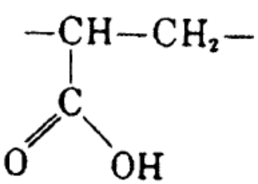
Poly(vinyl alcohol)

PVP



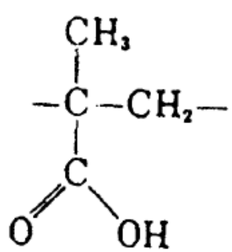
Polyvinylpyrrolidone

PAA



Poly(acrylic acid)

PMAA



Poly(methylacrylic acid

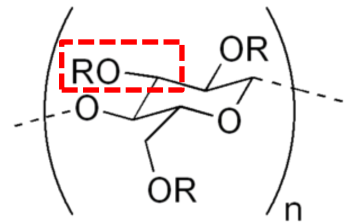
PEG $-CH_2-CH_2-O-$

Poly(ethylene glycol) and poly(ethylene oxide)

PEI $-CH_2-CH_2-NH-$

Polyethylenimine

Cellulose derivatives



CH_2-O-R groups

Methylcellulose	$-CH_2-O-CH_3$
Hydroxypropylmethylcellulose	$-CH_2-O-CH_2-CH(OH)-CH_3$
Hydroxyethylcellulose	$-CH_2-O-C_2H_4-O-C_2H_4-OH$ $-CH_2-O-C_2H_4-OH$
Sodium carboxymethylcellulose	$-CH_2-O-CH_2-C(=O)ONa$
Starches and dextrins	$-CH_2-OH$

Rahaman (2003), p. 353-356

Solvent Soluble Binders

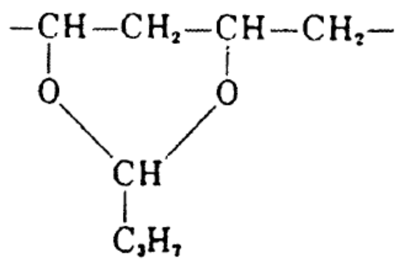
❑**With polar side groups:**

e.g., PVB, ethyl cellulose, PEG, PMMA

Vinyls

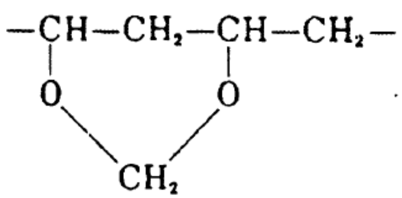
Poly(vinyl butyral)

PVB



Poly(vinyl formol)

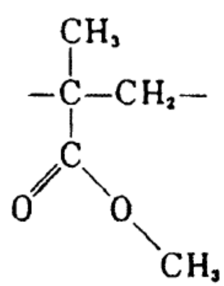
PVF



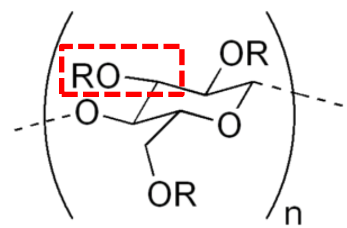
Acrylics

Poly(methyl methacrylate)

PMMA



Cellulose derivatives

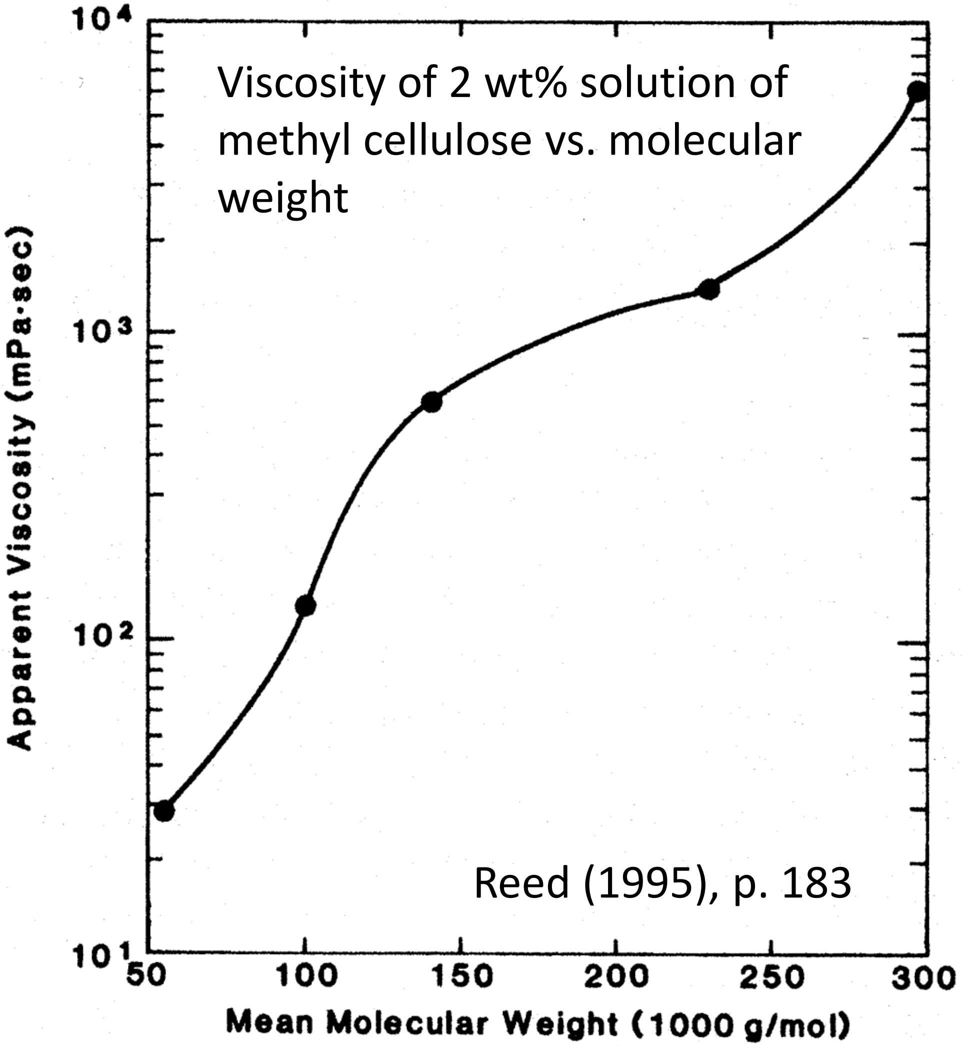


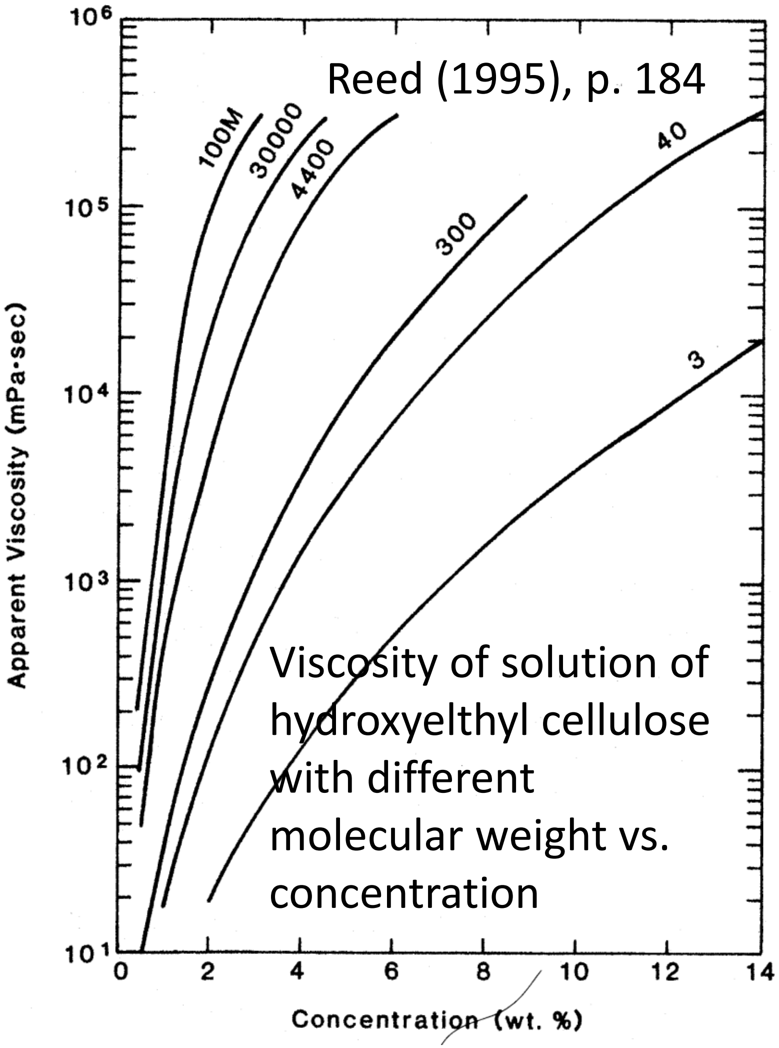
CH_2-O-R groups

Ethyl cellulose $-CH_2-O-CH_2-CH_3$

Binder Viscosity

❑Viscosity increases with concentration and molecular weight





Additional Effects of Binders

- **Plasticity**

  Binders often enable the plastic deformation of green body in forming process

- **Flocculation**

  Binders often lead to flocculation due to interaction between particles with adsorbed polymer binders

- **Thickening and Rheological Control**

  Binder addition to particle suspension may increase viscosity dramatically

- **Liquid retention**

  Binder adsorption reduce liquid migration, and the effect is significant for higher molecular weight polymer binders

Binder Selection

❑Selection criteria

- Burnout characteristics
  - Temperature
  - Inorganic residual
  - Atmosphere: air or inert
  - Volume change
- Molecular weight
  - Impacts viscosity and others
- Glass transition temperature
  - If too high Tg: green body too rigid
  - If too low Tg, green body too soft
- Compatibility with dispersant
  - Normally, binder should NOT displace dispersant so that in suspension become flocculated →Binder molecular should be LESS polar than dispersant
- Solubility in solvent
- Cost

Coagulents

❑Coagulation

Addition of agents, often electrolytes that reduce the expulsive force between charged surfaces of particles so that the particles come together, or coagulate

Examples

- Inorganic:
  - $CaCl_2$, $CaCO_3$, $MgCl_2$, or $MgSO_4$, etc.

Plasticizers (1)

❑Definition

Small (liquid) molecules added in small amount to plastics or thick particulate (including ceramics) pastes to cause the polymer (binder) to pack less densely and reduce the van der Waals forces binding the polymers together, which help softens the polymer (binder) and increase its flexibility (Reed (1995), p. 202-203)

"Plasticizer effectively reduces the **Tg** (glass transition temperature) of the polymer"

❑Example - (Adsorbed) water as plasticizer for PVA

	40% RH	60% RH	80% RH
Moisture content (wt.%)	5	9	17
Tensile strength (MPa)	67	44	35
Elongation at rupture (%)	17	195	240
Young's modulus (MPa)	435	175	88

Plasticizers (2)

❑Features

- Liquid with low vapor pressure (high boiling point) at the molding temperature
- Can be combined with water or other solvents
- Most plasticizer also increase water absorption

❑Common Plasticizer

	Melting point (^oC)	Boiling point (^oC)	MW (g/mol)
Water	0	100	18
Ethylene glycol	-13	197	62
Diethylene glycol (DEG)	-8	245	106
Triethylene glycol (TEG)	-7	288	150
Polyethylene glycol (PEG)	-10	>330	300
Glycerol	18	290	92
Dibutyl phthalate (DBP)		340	278

Melting & Glass Transition Temperatures for Polymer

- **Melting Temperature T_m**

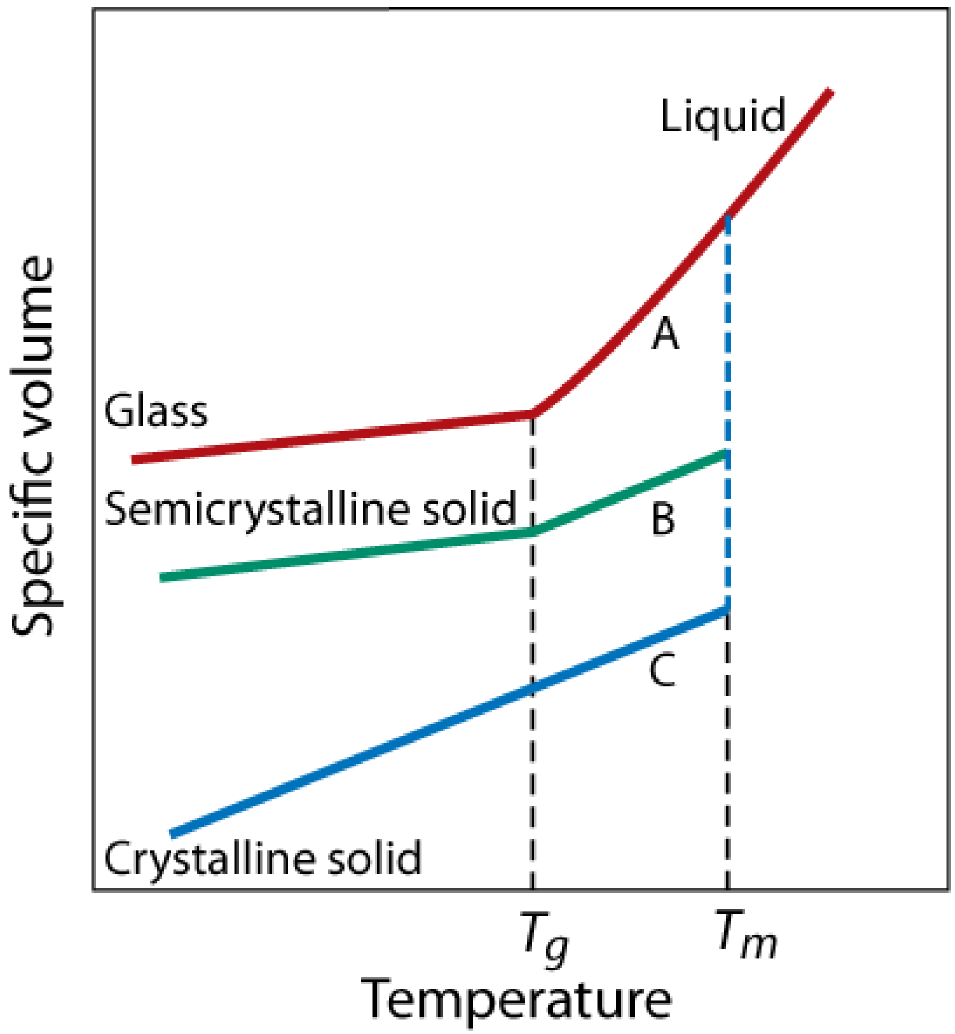
  For crystalline material, the temperature at which phase transition between (free-flowing) liquid and crystalline solid happen

- **Glass transition temperature, T_g**

  For glassy material, the temperature at which the highly viscous liquid transforms to rigid glassy solid, accompanied by sudden change in other physical/chemical properties (e.g. density)

- **T_m > T_g**

- **If Tg is too high**
  - At ambient temperature, polymer is glassy and rigid and brittle



Adapted from Fig. 15.18, *Callister & Rethwisch 8e, Wiley, 2009.*

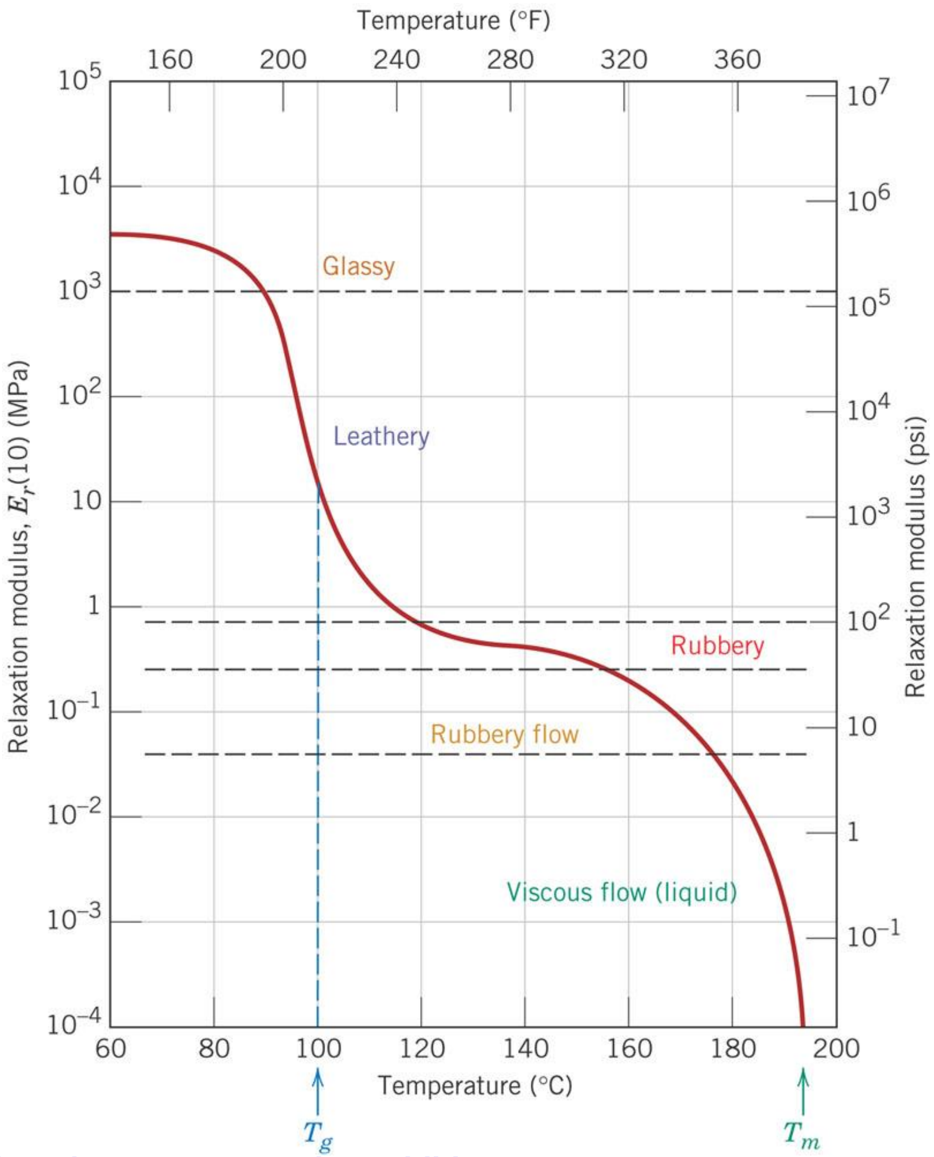
Modulus vs. Temperature for Polymers

Glass -
Rigid and brittle

Plastics -
Viscoelastic

Rubber –
Highly elastic

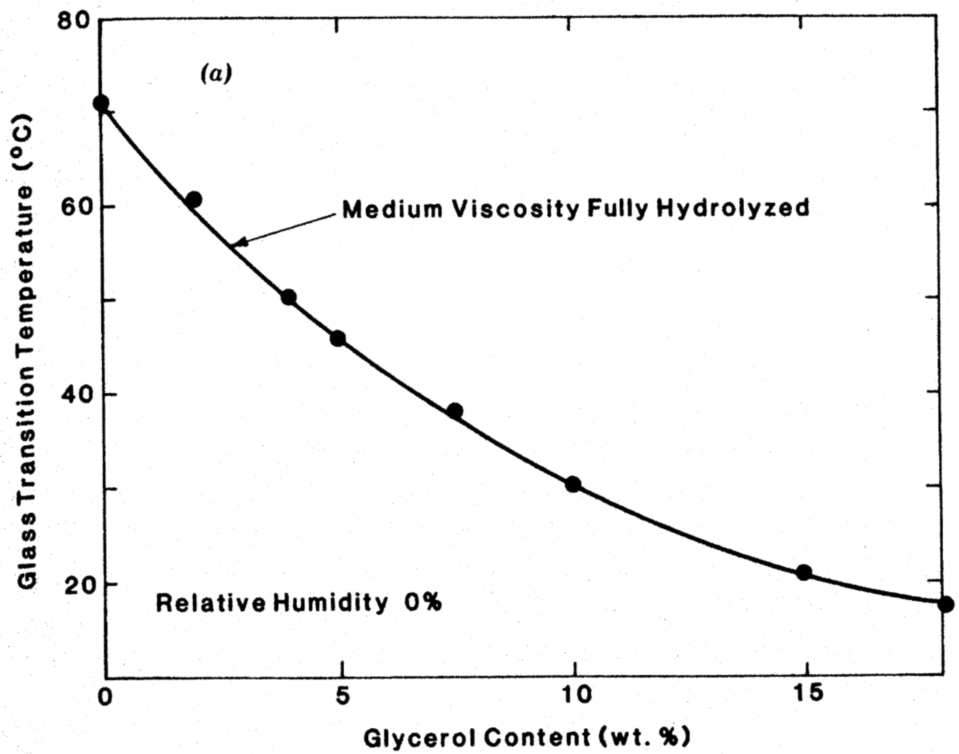
Polymer melts -
(Viscous)
flowing liquid



Adapted from Fig. 15.7, *Callister & Rethwisch 8e, Wiley, 2009.*

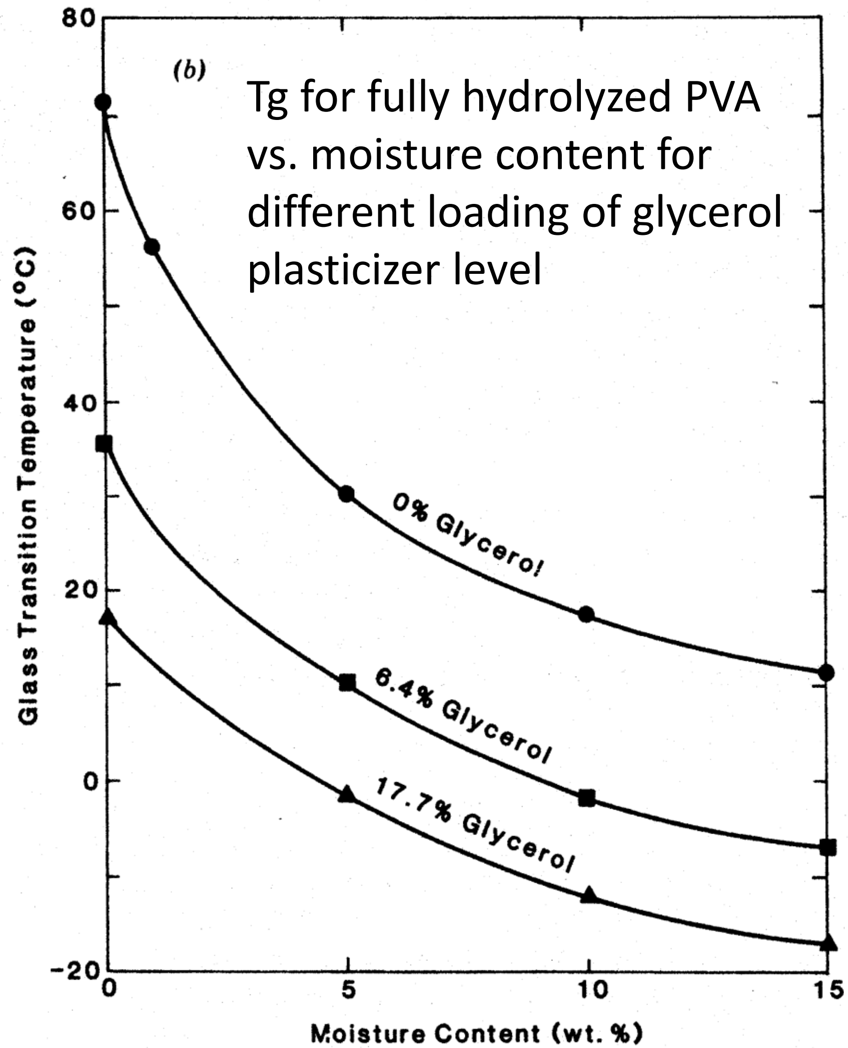
Examples of Plasticizer Effect on Tg

Tg for fully hydrolyzed PVA vs. glycerol plasticizer content with **no adsorbed moisture**



Reed (1995), p. 205

Tg for fully hydrolyzed PVA vs. moisture content for different loading of glycerol plasticizer level



Other Additives

❑Foaming agent

- Additive that reduces surface tension of solution (certain surfactant)
- Example:
  - Water has high surface tension, often leads to poor wetting and greater tendency towards foaming in milling → Change solvents (e.g., toluene) or add foaming agents such as tall oil; sodium alkyl sulfate; polypropylene glycol would help

❑Antifoaming agent

- Additive that offer very low surface tension (also certain surfactant)
- Examples:
  - Fluorocarbons; dimethysilicone; glycols

❑Lubricants

- Additive that reduces friction or resistance to sliding as in die compaction, injection molding, and extrusion.
- Examples:
  - Fluid lubricant: oil
  - Boundary lubricant: plasticized binder film such as stearic acid and salt
  - Solid lubricant: graphite; h-BN; MoS2; talc

Homework

- Identify in your own lab or if you don't have a lab Dr. Cheng lab the common additives of solvents, dispersants, binders, plasticizer, and other additives, if applicable
- Due Oct 12 class