

# **Ceramic Processing**

## **4 Processing Additives**



# 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

## □ 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



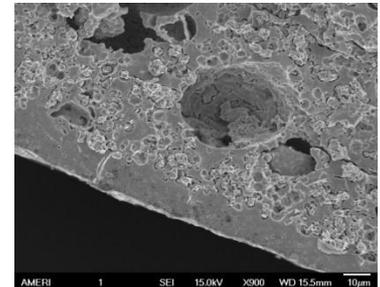
**Difference in flow capability**

<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**

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 (e.g., green tape before firing)

## ❑ 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 → used in most cases
- Good solvents for polar and ionic compounds
- Boiling point of 100 °C and melting point of 0 °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 18x10<sup>6</sup> Ω • cm) at 20 °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

Bahaman (2003), p. 345-347



# Organic Solvents

## ❑ Disadvantages compared with water

- Flammable or even explosive
- Volatile and giving vapor that is not only odorous, but also often hazardous
- May be toxic and difficult to dispose
- Expensive

## ❑ Use

- If ceramic powders are water reactive (e.g., BaTiO<sub>3</sub>, AlN, or Si<sub>3</sub>N<sub>4</sub>) or sensitive (e.g., LIB battery electrodes)
- To achieve very high solid loading (e.g., >80 wt%)
- For special applications that
  - Require higher solvent boiling point (e.g., screen printing using terpineol)
  - Require better wetting (e.g., thin film formation and printing using terpineol)
  - Require faster drying/higher evaporation rate (e.g., tape casting using toluene or MEK)
  - Avoid contamination and/or electrical shorting
- Trend - **gradual shift to more water-based systems**, whenever possible
  - Examples: paints, LIB electrode processing

## Ethanol (C<sub>2</sub>H<sub>5</sub>OH)

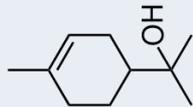


HEALTH	2
FIRE	3
REACTIVITY	0

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 <sub>2</sub> O	80	73	1.0	100	None
Methanol	CH <sub>3</sub> OH	33	23	0.6	65	18
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	24	23	1.2	79	8
Isopropanol (IPA)	C <sub>3</sub> H <sub>7</sub> OH	20	22	2.4	83	12
n-butanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH	18	25	2.9	118	35
Ethylene glycol (EG)	HOCH <sub>2</sub> CH <sub>2</sub> OH	37	48	16	197	111
Glycerol	HOCH <sub>2</sub> CHOHCH <sub>2</sub> OH	43	48	20	290	160
Acetone	CH <sub>3</sub> COCH <sub>3</sub>	21	22	0.3	56	-20
Methyl ethyl ketone (MEK)	CH <sub>3</sub> COCH <sub>2</sub> CH <sub>3</sub>	18	25	0.4	80	-9
Terpineol	C <sub>10</sub> H <sub>18</sub> O 	3	33	61	217	95
Trichloroethylene	CHCl=CCl <sub>2</sub>	3	29	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

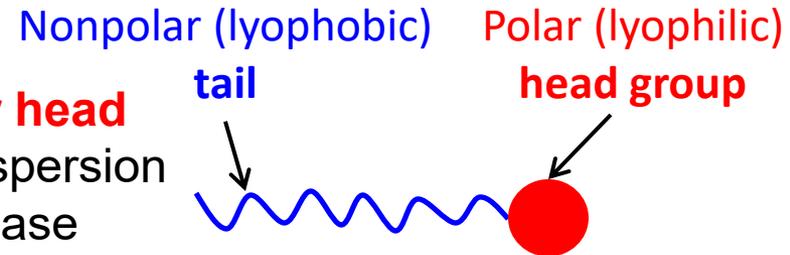
Molecules of special design that have one **polar head group** and a **nonpolar organic tail** that help dispersion of one phase (solid or liquid) in another liquid phase

## ☐ Two parts in a surfactant molecule

- **Nonpolar (hydrophobic/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/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 ( $-NH_2$ )

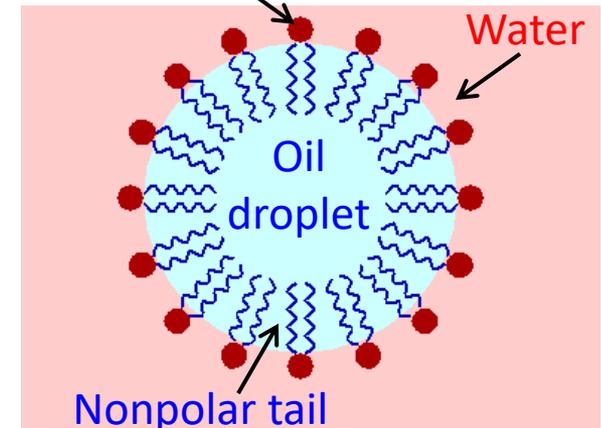
## ☐ Surfactant features

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



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

**Polar head group**



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

# 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 non-polar (hydrophobic) tail

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

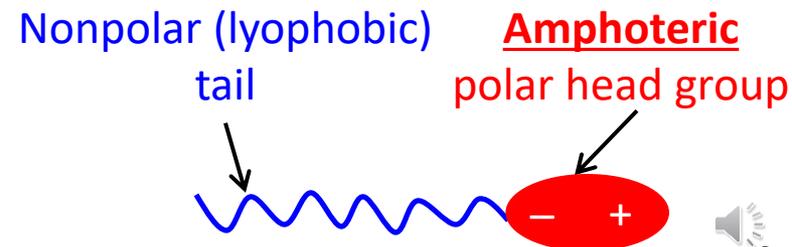
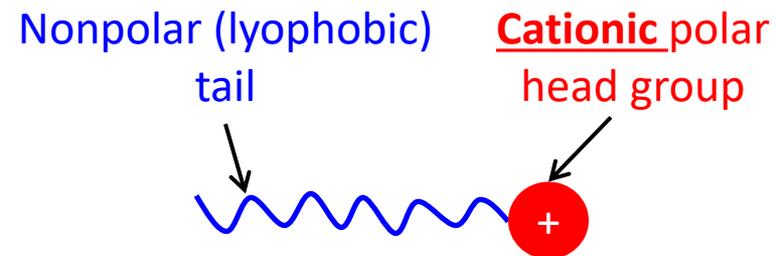
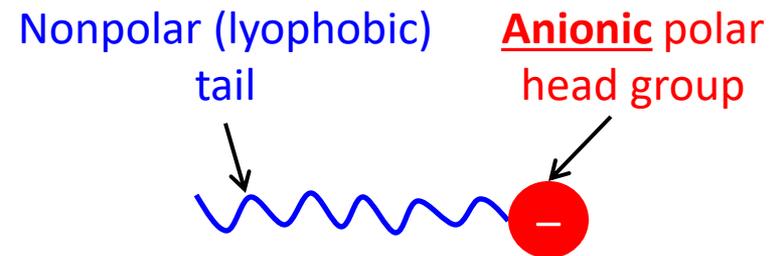
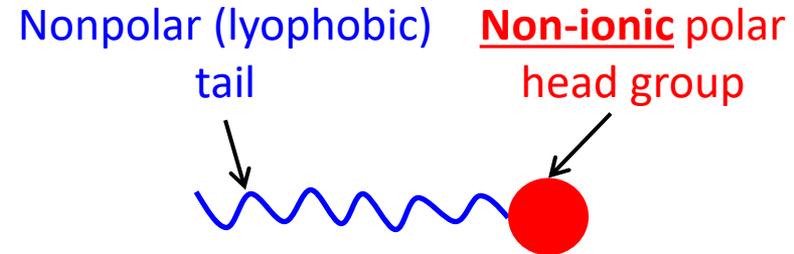
## ❑ Cationic surfactant

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

- Tends to adsorb on surface negative particles

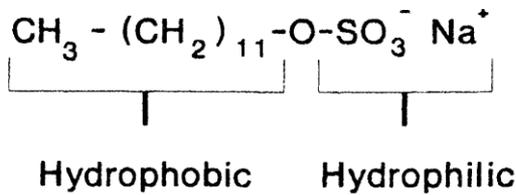
## ❑ Amphoteric surfactant

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



(OCTYLPHENOXYPOLYETHOXYETHANOL)  
NON-IONIC SURFACTANT

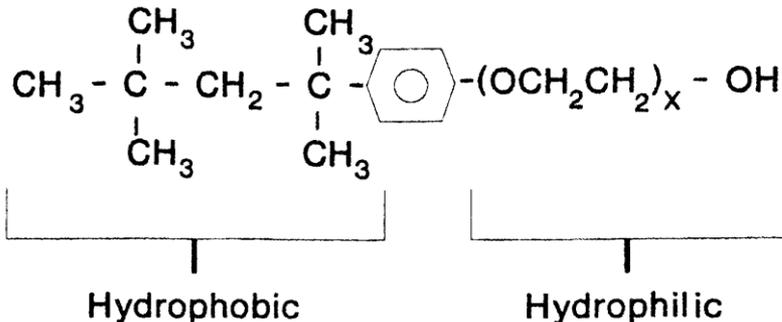
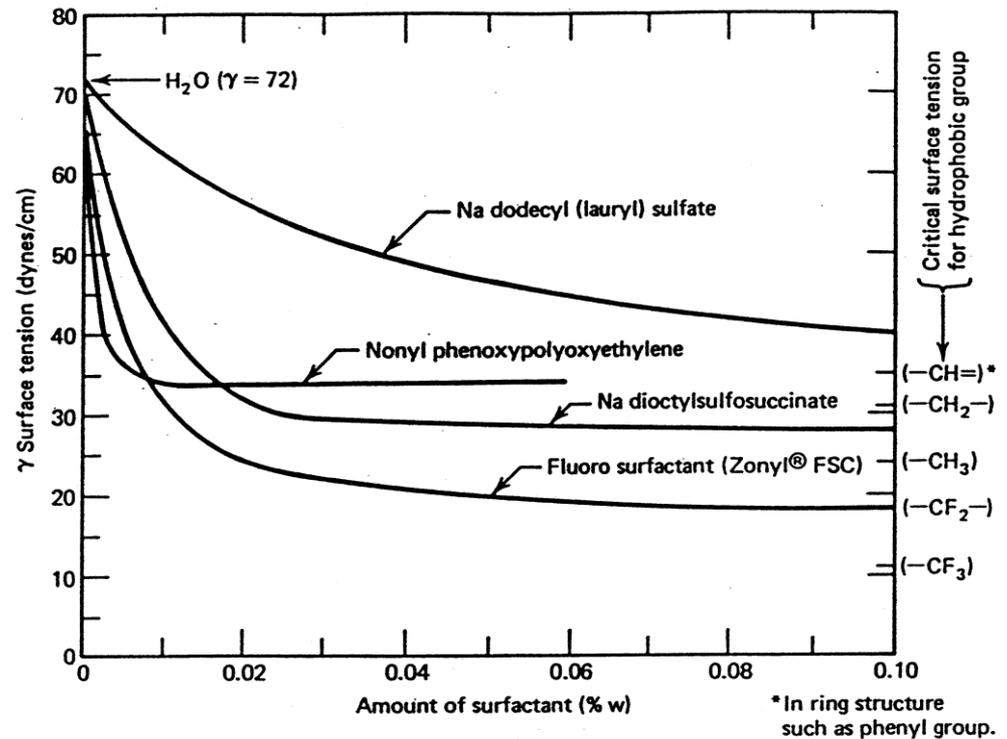


TABLE 9.4 Examples of Surfactants

Type	Generic Name	Composition
Nonionic	Ethoxylated nonylphenol	$\text{C}_9\text{H}_{19}(\text{C}_6\text{H}_4)\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}$
	Ethoxylated tridecyl alcohol	$\text{C}_{13}\text{H}_{27}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{12}\text{H}$
Anionic	Sodium stearate	$\text{C}_{17}\text{H}_{35}\text{COO}^- \text{Na}^+$
	Sodium disopropylnaphtalene sulfonate	$(\text{C}_3\text{H}_7)_2\text{C}_{10}\text{H}_5\text{SO}_3^- \text{Na}^+$
Cationic	Dodecyltrimethylammonium chloride	$[\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_3]^+ \text{Cl}^-$



# 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 <sub>4</sub> <sup>-</sup> Na <sup>+</sup>	39.0
-COO <sup>-</sup> K <sup>+</sup>	21.0
-COOH	2.1
-OH	1.9
-O-	1.3
-CH <sub>2</sub> -	0.47
-CH <sub>3</sub>	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

# 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](http://sc.akzonobel.com/en/fabric-cleaning/Documents/AkzoNobel_tb_HlbEmulsions.pdf)

# Low to Medium Molecular Weight Polymers as Dispersants (1)

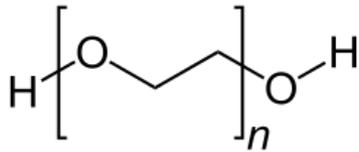
## ❑ Description

Polymer dispersants with molecular weight of several hundred to several thousand

## ❑ Non-ionic

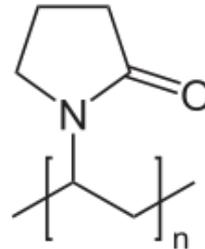
### PEG

Polyethylene glycol



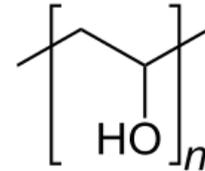
### PVP

Poly vinyl pyrrolidone



### PVA

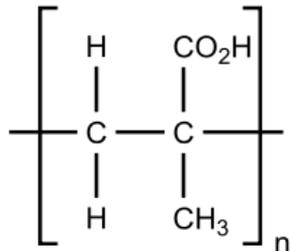
Poly vinyl alcohol



## ❑ Ionic (also called polyelectrolytes)

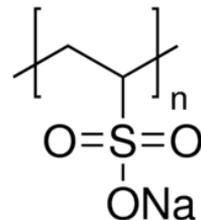
### PMAA

Poly methacrylic acid



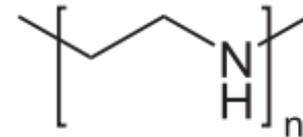
### PVSA

Poly vinylsulfonic acid



### PEI

Polyethyleneimine



# Low to Medium Molecular Weight Polymers as Dispersants (2)

## □ Feature

- Solubility depend on chain side groups:
  - -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

# Simple Inorganic Ions and Molecules as Dispersants

## □ For aqueous suspension

Simple ions and molecules can be effective dispersants and they are 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

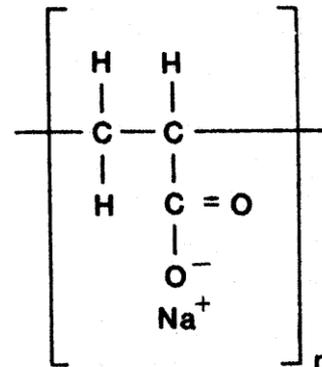
### ▪ Examples:

- For oxides:

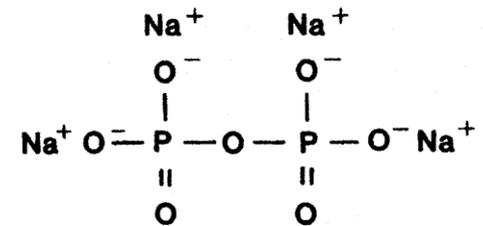
- Tetrasodium pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7$ );
- Sodium carbonate ( $\text{Na}_2\text{CO}_3$ )
- HCl

- For clays

- Disodium silicate ( $\text{Na}_2\text{SiO}_3$ )



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

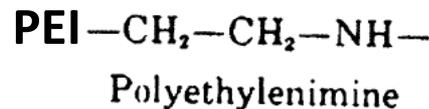
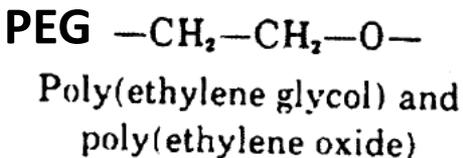
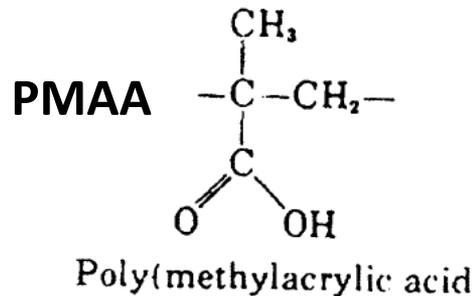
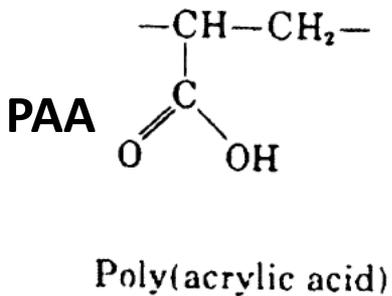
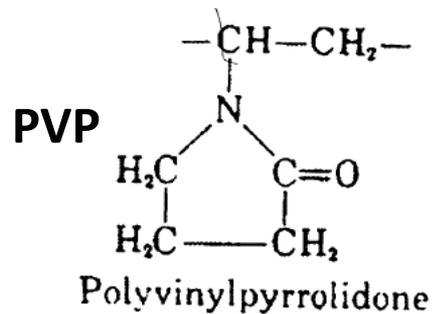
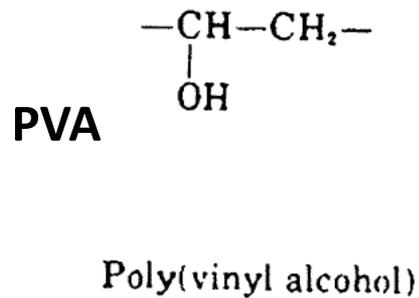
	Organic	Inorganic
Colloidal	Microcrystalline cellulose	Kaolin clay
Molecular	Natural gum (e.g., gum arabic)	Soluble silicate (e.g., $\text{Na}_2\text{O} \cdot (\text{SiO}_2)_n$ )
	Polymerized alcohols (e.g., polyvinyl alcohol PVA)	Organic silicate (e.g., $\text{Si}(\text{OC}_2\text{H}_5)_4$ )
	Polymerized butyral (e.g., polyvinyl butyral or PVB)	Soluble phosphates (e.g., $\text{Na}_3\text{PO}_4$ )
	Cellulose ethers (e.g., ethyl cellulose EC)	Sodium aluminate (e.g., $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$ )
	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](http://digitalfire.com/4sight/education/binders_for_ceramic_bodies_345.html)

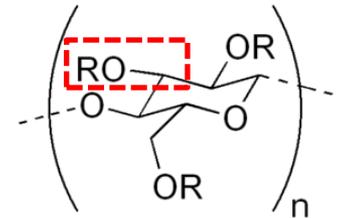
# Water Soluble Binders

□ With polar side groups:

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



## Cellulose derivatives



**CH<sub>2</sub>-O-R (R group polar)**

Methylcellulose	$\text{—CH}_2\text{—O—CH}_3$
Hydroxypropylmethylcellulose	$\text{—CH}_2\text{—O—CH}_2\text{—CH—CH}_3$   OH
Hydroxyethylcellulose	$\text{—CH}_2\text{—O—C}_2\text{H}_4\text{—O—C}_2\text{H}_4\text{—OH}$ $\text{—CH}_2\text{—O—C}_2\text{H}_4\text{—OH}$
Sodium carboxymethylcellulose	$\text{—CH}_2\text{—O—CH}_2\text{—C} \begin{array}{l} \text{// O} \\ \text{\backslash ONa} \end{array}$
Starches and dextrans	$\text{—CH}_2\text{—OH}$

Rahaman (2003), p. 353-356

# Solvent Soluble Binders

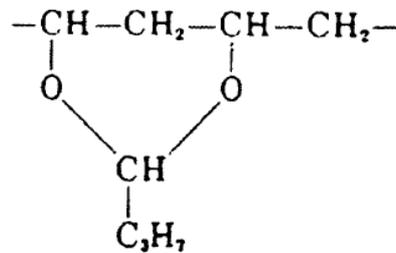
## □ With non-polar side groups:

e.g., PVB, ethyl cellulose (EC), PVF, PMMA

### Vinyls

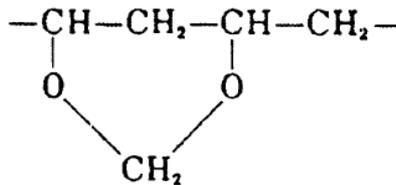
Poly(vinyl butyral)

**PVB**



Poly(vinyl formol)

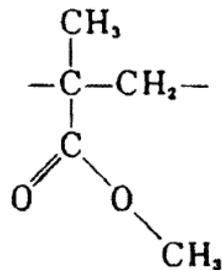
**PVF**



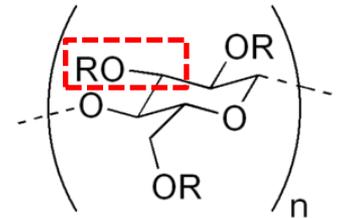
### Acrylics

Poly(methyl methacrylate)

**PMMA**

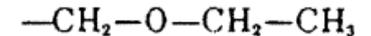


### Cellulose derivatives



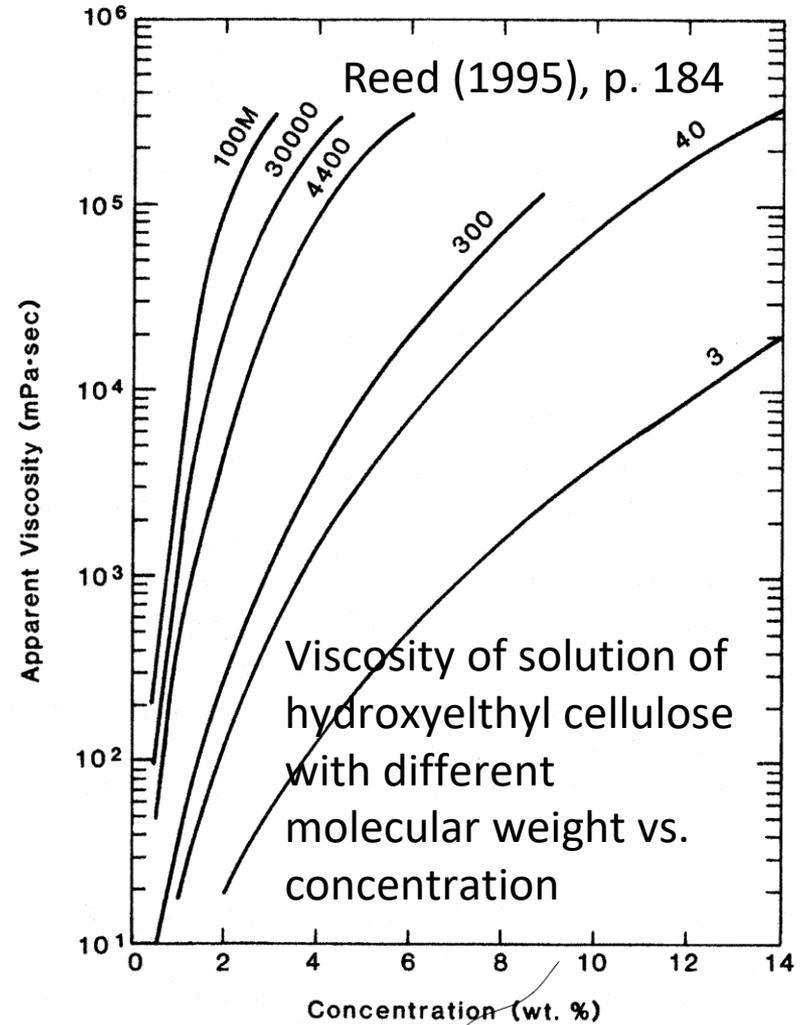
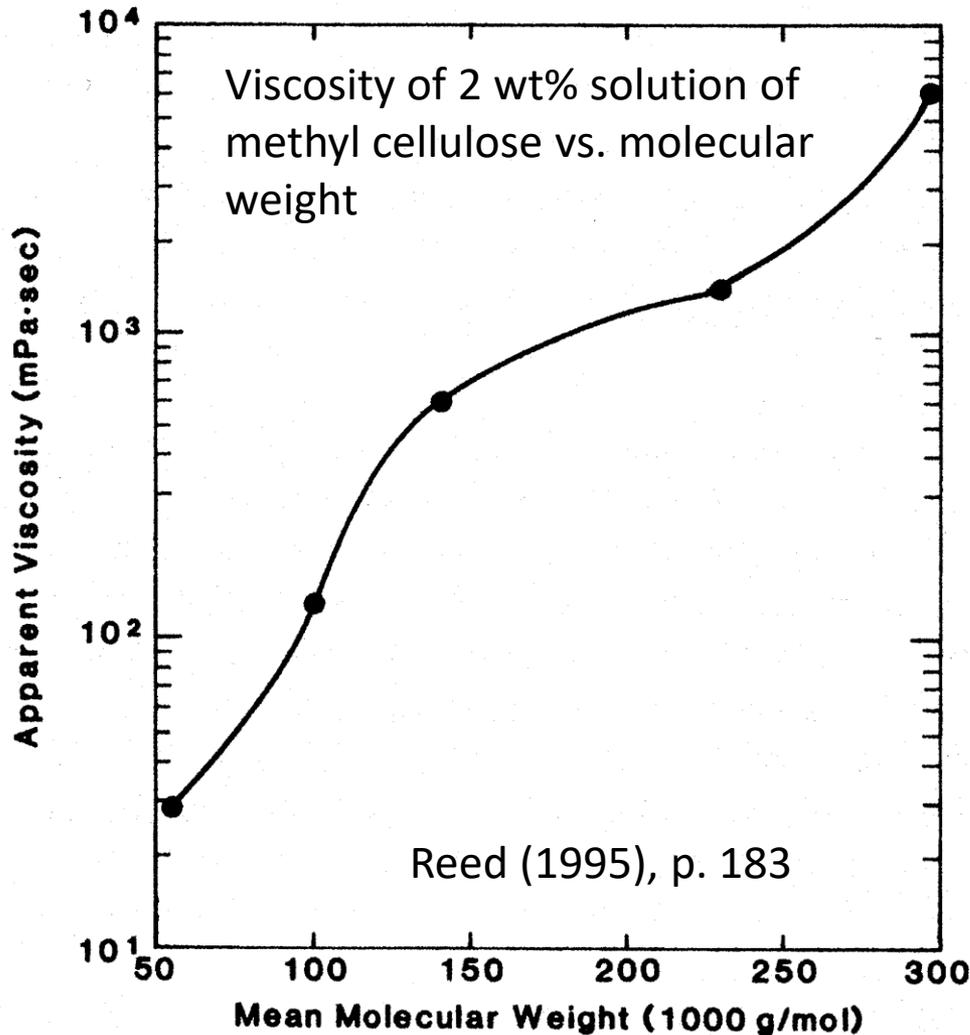
Ethyl cellulose

**CH<sub>2</sub>-O-R (R group non-polar)**



# Binder Viscosity

□ Viscosity increases with binder molecular weight & concentration



# Additional Effects of Binders

## ❑ Plasticity

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

## ❑ Flocculation

Binders often lead to flocculation in suspension 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  $T_g$ : green body too rigid
  - If too low  $T_g$ , green body too soft
- Compatibility with dispersant

Normally, binder should NOT displace dispersant so that 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 repulsive force between charged surfaces of particles so that the particles come together, or coagulate

Examples

- Inorganic:
  - $\text{CaCl}_2$ ,  $\text{CaCO}_3$ ,  $\text{MgCl}_2$ , or  $\text{MgSO}_4$ , 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

“Plasticizer effectively reduces the **T<sub>g</sub>** (glass transition temperature) of the polymer”

## □ Example – Effect of relative humidity (RH) and, as a result, adsorbed water as the plasticizer for PVA film’s mechanical properties

	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 plasticizers

	Melting point (°C)	Boiling point (°C)	MW (g/mol)
Water	0	100	18
Ethylene glycol (EG)	-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 Point ( $T_m$ ) & Glass Transition Temperature ( $T_g$ ) for Polymer

## ❑ Melting Temperature $T_m$

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

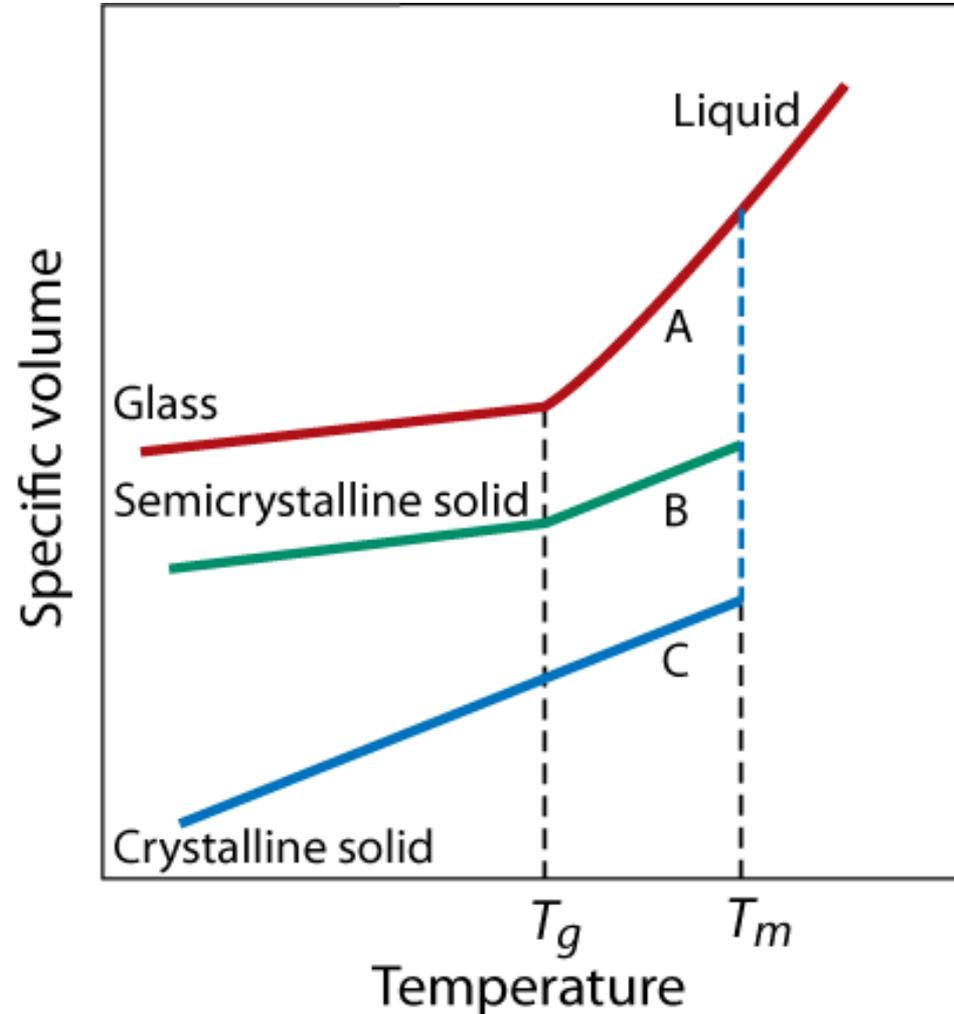
## ❑ Glass transition temperature $T_g$

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 $T_g$ is too high (above RT)

- At ambient temperature ( $\sim 20^\circ\text{C}$ ), polymer is glassy - rigid & brittle



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

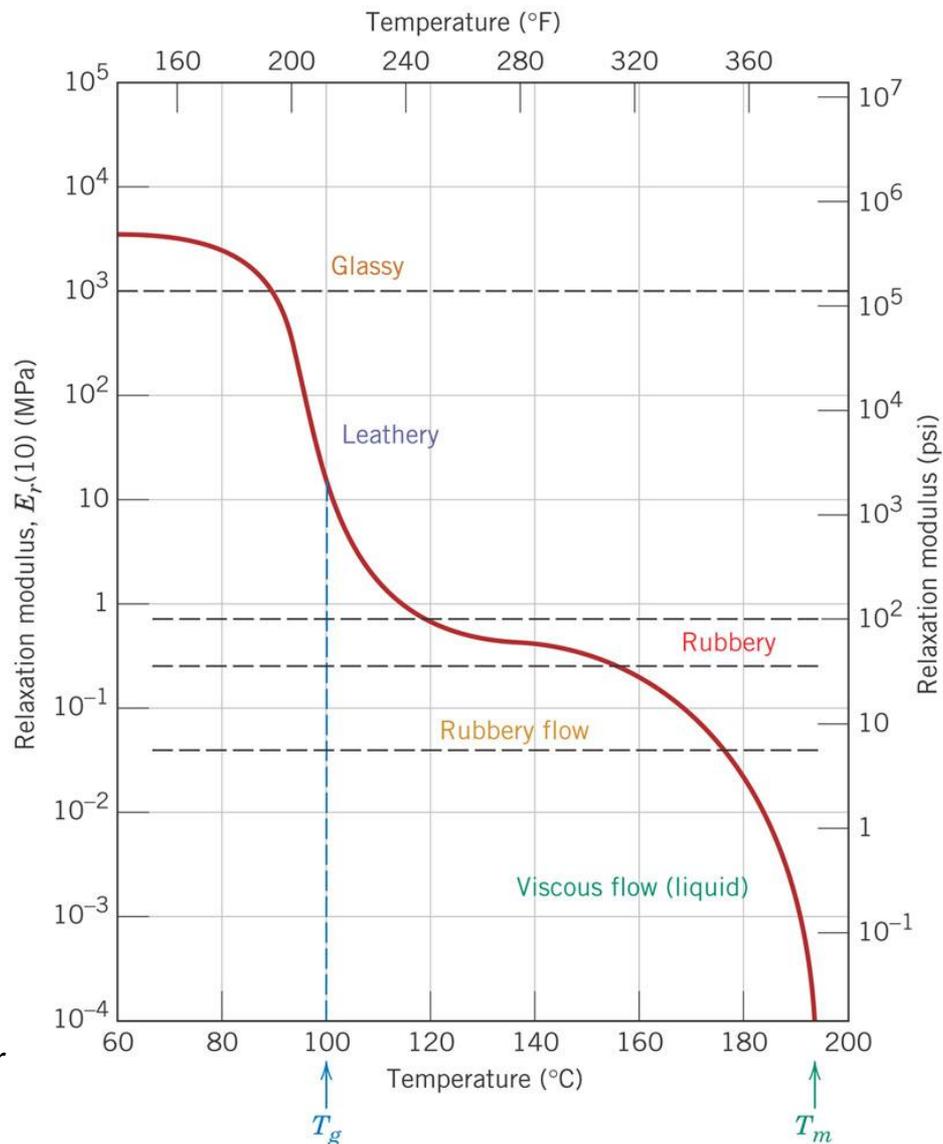
# Modulus vs. Temperature for Polymers

Glass -  
Rigid and brittle

Plastics -  
Viscoelastic

Rubber -  
Highly elastic

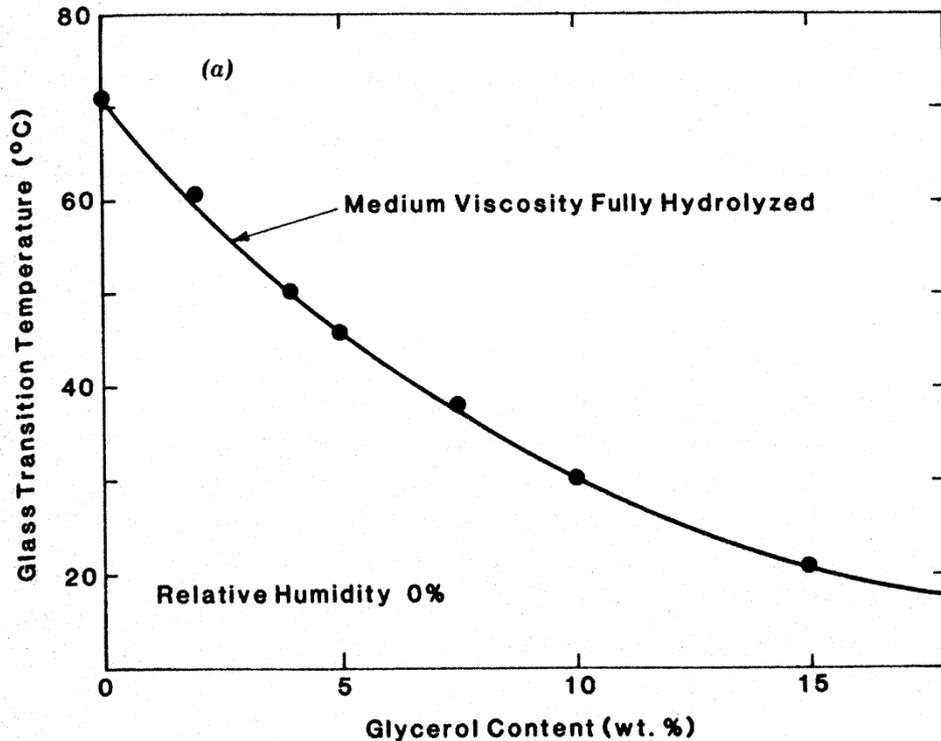
Polymer melts -  
(Viscous)  
flowing liquid



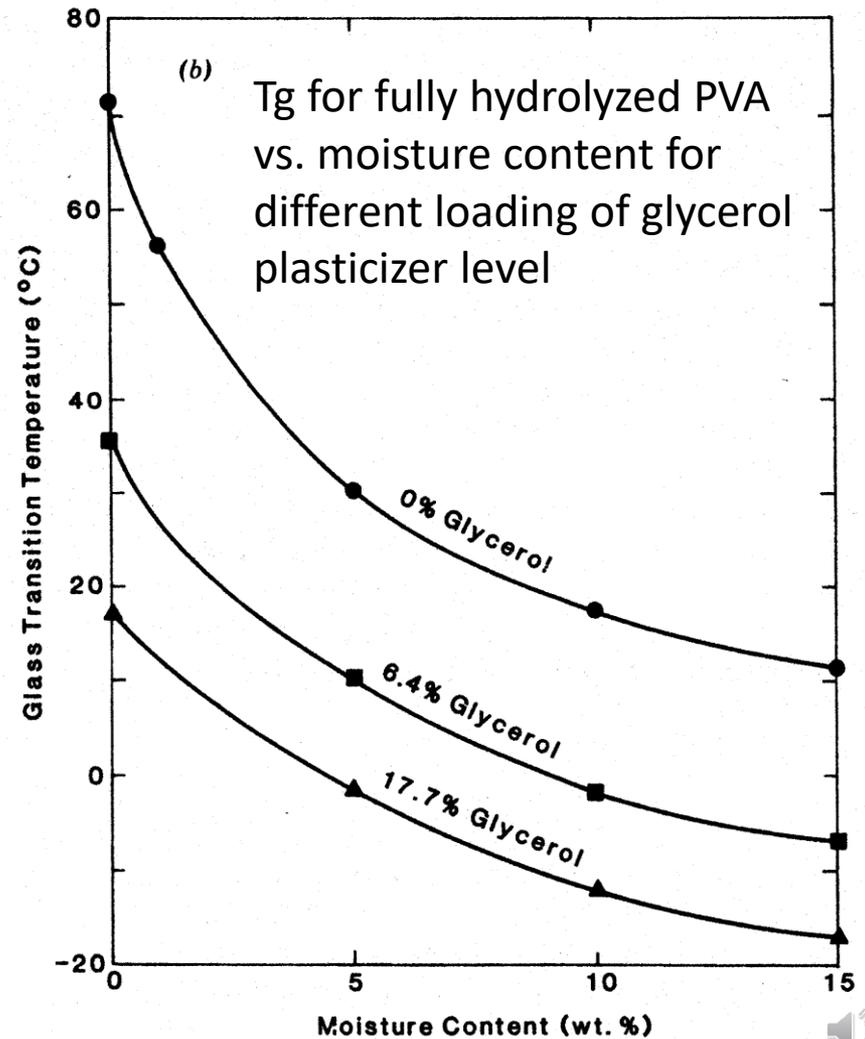
Adapted from Fig. 15.7, Callister & Rethwisch 8e, Wiley, 2009.

# Examples of Plasticizer Effect on $T_g$

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



Reed (1995), p. 205



# 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; dimethylsilicone; 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; MoS<sub>2</sub>; 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

