Overview of polymer coatings (paint and other coatings)

Pigment volume concentration (PVC and CPVC)
Rheology
Crosslinking and film strength
Powder coatings

Latex coatings

Viscosity and colloidal stability
Emulsion polymerization
Particle morphology

How latex particles form films:
Drying, deformation, and contact (and VOCs)
Lecture 2

Latex Coatings and Latex Film Formation

- Polymer diffusion and development of mechanical strength
- Brief introduction to ET (non-radiative energy transfer)
- Brief introduction to SANS (small angle neutron scattering)
- Polar membranes in latex films
- Moisture and humidity effects

Required reading will be posted on the course web site.
Polymer Coatings (paint)

The resin is a glue holding the paint together cohesively and providing adhesion to the substrate. The resin is always a polymer.
Nanomaterials used in coatings

The coatings industry is the largest producer and consumer of nanoparticles in the world.

Examples:

- Monodisperse polymer particles, $d = 80 \text{ nm to } 400 \text{ nm (megatons per year)}$
- TiO$_2$ Pigment, $d = 450 \text{ nm}$
- Al$_2$O$_3$ shell, $d = 450 \text{ nm}$
- Hollow PS-PMMA crosslinked beads, $d = 450 \text{ nm}$
- Rhopaque™
some terms:

Protective coatings: The primary function of these coatings is to protect the underlying substrate. At the very high-tech end are automotive recoat paints.

Decorative coatings: The primary function is to hide the surface or previous coating. Interior house paints are the most common example.

Varnish (clear coat) has no pigment.

“100% solids” has no solvent.

Lacquers are high M polymers dissolved in a solvent. They dry to leave an entangled plastic film.

VOC (volatile organic content): wt/unit volume of most organic compounds with bp \( \leq 250 \) C.
Pigmented coatings

Pigments provide opacity and color to a coating. The TiO₂ particle size is chosen to give the maximum scattering of visible light. It is the normally the most expensive component in the coating.

Other pigments in smaller amounts give color to the coating.

The TiO₂ used as a pigment in coatings is covered by a thin layer of silica (or alumina) to prevent photo-oxidation of the matrix.

In paper coatings, clay and calcium carbonate are commonly used in coatings. The volume fraction of pigment is much higher than in paints.
PVC and film properties

PVC (pigment volume concentration)
CPVC (critical PVC): the concentration of pigment at which the pigment becomes continuous and there is just enough binder to fill the interstitial spaces.

High gloss coatings have low PVC.

At PVC > CPVC, the film contains voids.

Coating Rheology

viscosity as a function of shear rate

Thixotropic flow is a special type of pseudoplastic flow typical of most coatings. As shear rate is increased, the viscosity drops. As the shear rate is decreased back to zero, the viscosity builds more slowly. The time to regain full structure (sec to hr) is vital to coating rheology because it relates to properties such as sag resistance, film build, flow and leveling.

A variety of soluble polymers are added to the paint formulation as rheology modifiers.

ENTANGLEMENTS -- Review

For many polymers, it has been observed that above a critical molar mass ($M_e$), the melt viscosity increases as $M^{3.4}$. This behavior is attributed to the effect of entanglements.

The confining effect of the surrounding chains act like a confining tube.

Graessley, 1974; taken from Tonelli, AE Polymers from the Inside Out, Wiley, 2001 p 139
film strength as a function of molar mass (for polystyrene)

Cohesive strength of a coating

Definition of tensile strength and fracture energy

The initial slope is the modulus.

Solutions of polymers with \( M >> M_e \) have very high viscosity and have to be applied at low solids.

from R. Wool, *Polymer Interfaces*, 1997
Thermoset coatings

Many coatings that cure are low M polymers with reactive groups dissolved in a solvent. They dry to form a weak plastic film that undergoes crosslinking on the substrate.

- Oxidative cure: alkyds
- Moisture cure: alkoxy silanes, silicates
- “2-pack” (“2K”): epoxy + curing agent, urethane
- Baking systems: melamine, N-methylol acrylamide + acid

After crosslinking, the entire film becomes a single interconnected molecule.
Thermoset coatings

Crosslinked coatings have better solvent resistance, better acid and base resistance. They have improved hardness and tensile strength, often at the expense of brittleness.

Parameters characterizing crosslinked coatings.
1. gel content \((1 - \text{sol content})\)
2. crosslink density (mean chain length \(M_c\) between crosslinks)
3. Swell ratio when exposed to a solvent
Powder coatings melt (soften and flow) when they are heated, and crosslink as the particles fuse into a film. These are pigmented coatings.
The bed can be charged from an overhead electrode. The object (grounded) within the cloud of electrostatically charged powder is more uniformly coated.

Electrostatically charged beds eliminate the need for pre-heating the object and reduce the quantities of powder needed.
Adhesion and cohesion in multilayer coatings

Automotive coatings:
clear coat (gloss, UV protection)
basecoat (pigment)
primer

Examples of paint failure

A latex is a colloidal dispersion (suspension) of polymer particles in water.

Latex particles consist of polymer molecules of any molar mass (typically 5000 to $1 \times 10^6$).

Latex dispersions maintain low viscosity for high solids even for high M polymers.

Colloidal stability is either coulombic or steric in origin.

Coulombic (charge) stabilization

Steric (entropic) stabilization
Aqueous polymer dispersions by class

- styrene-butadiene, 37%
- vinyl acetate, 28%
- acrylate, 30%
- other, 5%

Fig. 1-2  What is a polymer dispersion?

from D Urban, K Takamura, Eds.  
Polymer Dispersions and their Industrial Applications. Wiley-VCH 2002
MECHANISMS FOR COLLOIDAL STABILITY

Electrostatic Stabilization

Steric Stabilization

Aqueous dispersions must maintain colloidal stability during storage but lose this stability at some key point during the application.
EMULSION POLYMERIZATION

- Surfactant
- Micelle
- Monomer
- Water
- Surfactant
- Initiator
- Monomer droplets

Diagram shows a flask with monomer droplets, water, surfactant, and an initiator.
Typical acrylate monomers

methyl methacrylate (MMA)

2-ethylhexyl acrylate (EHA)

butyl methacrylate (BMA)

butyl acrylate (BA)

In North America, the most common latex for paints are copolymers of BA with MMA or BA with vinyl acetate (VAc).
EMULSION POLYMERIZATION

Tab. 2-1 Model system for the study of some aspects of emulsion polymerization.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity (phm)</th>
<th>Influence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100–150</td>
<td>Solids content; viscosity</td>
</tr>
<tr>
<td>Styrene</td>
<td>0–95</td>
<td>Glass transition temp; minimum film-forming</td>
</tr>
<tr>
<td><em>n</em> -Butyl acrylate</td>
<td>0–95</td>
<td>Glass transition temp; minimum film-forming</td>
</tr>
<tr>
<td>Methacrylic acid</td>
<td>0–5</td>
<td>Colloidal stability; viscosity; reaction kinetics</td>
</tr>
<tr>
<td>Sodium lauryl sulfate</td>
<td>0.5–3.0</td>
<td>Particle size; colloidal stability; reaction kinetics</td>
</tr>
<tr>
<td><strong>SDS</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium persulfate</td>
<td>0.1–1.0</td>
<td>Particle size; colloidal stability; reaction kinetics; molecular wt.</td>
</tr>
<tr>
<td>C_{12}H_{25}-SH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t- Dodecyl mercaptan</td>
<td>0–1.0</td>
<td>Molecular wt.; reaction kinetics</td>
</tr>
<tr>
<td>Divinylbenzene</td>
<td>0–0.5</td>
<td>Cross-linking/gel</td>
</tr>
</tbody>
</table>

1 Parts per hundred parts of monomer
EMULSION POLYMERIZATION

Stage 1: Particle nucleation (homogeneous or micellar)
Stage 2: Particle growth fed by monomer from the monomer droplets
   (Transport of the monomer through the aqueous phase is critical.)
Stage 3: Particle growth after disappearance of the monomer droplets
For most monomers

Initiation occurs in the water phase.

Polymerization occurs in the water phase and in the particles.

When oligomers formed in the water exceed their solubility, they are “swept up” by the growing particles.
“Protective Colloid”

<table>
<thead>
<tr>
<th>ingredient</th>
<th>amount, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>vinyl acetate</td>
<td>16.0</td>
</tr>
<tr>
<td>dibutyl maleate</td>
<td>4.0</td>
</tr>
<tr>
<td>poly(vinyl alcohol) 10%</td>
<td>10.0</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.200</td>
</tr>
<tr>
<td>H₂O</td>
<td>69.8</td>
</tr>
<tr>
<td>KPS</td>
<td>0.200</td>
</tr>
</tbody>
</table>

When emulsion polymerization is carried out in the presence of a water-soluble polymer, the polymer becomes grafted to the particle surface.

When the polymer at the particle surface is a polyelectrolyte, the particle is said to be “electro-sterically stabilized.”

The grafted polymer is called a steric stabilizer. In the old literature, the polymer itself is referred to as a “protective colloid.”

PVOH partially hydrolyzed PVAc
If the reactivity ratios are unfavorable, the composition changes throughout the reaction, and phase separation occurs.

Example: VAc-BA copolymerization ($r_{\text{VAc}} \approx 0.02; r_{\text{BA}} \approx 3$) The VAc radical prefers to add BA, and the BA radical also prefers to add BA. The BA monomer is used up first, followed by the VAc.
When the reactivity ratios are unfavorable, particles with uniform polymer compositions can be prepared by seeded semi-continuous emulsion polymerization under “monomer-starved” conditions.
If the second stage monomer is different than the first, one can obtain structured latex particles.

**Fig. 3-15  Morphologies of polymer particles.**

These morphologies can be very useful for obtaining unique properties: crosslinked core, hard core-soft shell, soft core-hard shell.
Questions

1. Imagine that you have a sample of monodisperse PMMA particles with a diameter of 200 nm and the polymer has $M_n = 100,000$, $M_n / M_w = 3$. On average, how many polymer molecules are there per particle?

2. Imagine that you have a sample of monodisperse polystyrene with $M_n = 20,000,000$ and that you can emulsify them to produce particles containing a single molecule. What would be the diameter of the particles? How does the particle radius compare to the unperturbed radius of gyration of PS? What would you expect to happen if you melt-pressed a film of these particles and annealed them at $T >> T_g$ (PS)?
Environmental factors are causing major changes in the coatings industry.

• replacement of solvent-borne coatings by waterborne coatings (low VOC)
• removal of all solvent from waterborne coatings (e.g., 15 wt% organic solvent)

Most waterborne coatings involve latex dispersions.

A latex is defined as a dispersion of polymer nanoparticles in water.
LATEX FILM FORMATION PROCESS

latex in water
solids content 40 to 50 wt%
particles in contact
void-free solid
mechanically coherent film

drying
water evaporates
particles deform
T > MFT

diffusion
polymer diffusion
mechanically coherent film
How latex dispersions dry on a substrate

Water evaporates most rapidly at the dry/wet boundary. There is a flux of water and particles toward the edge of the film.
The polymer modulus must be less than $10^7$ Pa. Deformation precedes contact during the drying process.

The MFT is the minimum temperature at which the latex will form a transparent film on drying.
LATEX FILM FORMATION

Forces associated with drying deform latex spheres into space-filling polyhedral cells.

Capillary forces, surface tension....
If the particles in solution form a colloidal crystalline phase, with fcc packing, isotropic deformation will lead to rhombic dodecahedra.

Isotropic compression should lead to shrinkage in the x,y plane.
LATEX FILM FORMATION

Isotropic deformation of fcc packed particles will lead to rhombic dodecahedra.

Freeze-fracture TEM images of a poly(butyl methacrylate) latex film.

PBMA $d = 337$ nm
20 h at 36 °C
Freeze-fracture TEM images of a poly(butyl methacrylate) latex film.

PBMA 337 nm
20 h at 36 °C
rhombic dodecahedra

Interfacial fracture in the new film.

Cohesive fracture after annealing.

2 h, 80 C

surfactant (SDS) crystals.
LATEX FILM FORMATION

Drying

Plasticizers lower Tg and decrease the modulus.

The polymer modulus must be less than 10^7 Pa

volatile plasticizers (VOC)

\[
\begin{align*}
\text{TMP (Texanol)} & \quad \text{butyl carbitol} \\
\text{butyl cellosolve} &
\end{align*}
\]

If an organic solvent is added to the latex and dissolves in the particles, it will act as a plasticizer.

\[
\frac{1}{T_g} = \frac{w_{\text{pol}}}{T_{g,\text{pol}}} + \frac{w_{\text{solv}}}{T_{g,\text{solv}}}
\]

Fox equation
LATEX coatings

Volatile solvents added to the dispersion, lower the modulus of the polymer in the particles.

After the paint dries on the substrate, the solvents evaporate and the Tg of the polymer increases.

But this releases VOCs into the atmosphere.

The polymer modulus must be less than $10^7$ Pa

Volatile plasticizers (VOC)
- TMP (Texanol)
- Butyl carbitol