CHEM 470
Polymers in Personal Care Products

While surfactants may be considered workhorse materials in the cosmetic industry, polymers are certainly the most versatile. Used in small concentrations, polymers can create a full range of effects in formulations, from thickening to preservation to conditioning.

I. Chemistry
   a. Homopolymer – one type of monomer
   b. Copolymer – two or more types of monomers
   c. Linear or branched
      i. Branched polymers generally have lower density than linear, and linear polymers are used most often in cosmetic formulations
   d. Natural polymers
      i. Polysaccarides, proteins, nucleic acids
      ii. Polysaccarides are used most often in cosmetic preparations, including cellulose, starch, chitin, xanthan gum and guar gum
      iii. Gelatin, collagen, soy bean, silk and milk are examples of natural protein polymer sources
         1. generally not suitable for use in cosmetic formulations without chemical modification
   e. Synthetic polymers
      i. Monomers: acrylic acid, vinyl pyrrolidone, ethylene oxide or propylene oxide
      ii. Polyesterification: diol + diacid → polymer with an acid and alcohol functionality that can react further
      iii. Chain-reaction polymerization, also called addition reactions
   f. Side groups
      i. Affect physical properties
         1. molecular weight, polymer structure, viscosity, solubility, transition temperatures
         2. how well the polymer thickens, conditions and forms films
   g. Structure
      i. Crystalline or amorphous
         1. generally, amorphous polymers used most often in cosmetic formulations
      ii. monodisperse (mixture of polymer strands with uniform molecular weight)
      iii. polydisperse (a mixture of polymer strands that have a range of molecular weights)
      iv. viscosity
      v. solubility and transition temperatures

1. aqueous or nonaqueous
2. polysorbates – emulsifiers
3. transition temperatures (solid – liquid – gas)
4. amorphous polymers have additional transition temperature → glass transition temperature (T_g)
5. T_g – temperature at which there is an absorption or release of energy as the temperature is raised or lowered
    a. Important for polymers used in styling products

II. Styling polymers
- a. Conditioning, humectancy, thickening and opacity functions, preservation, and foam stabilizing
- b. Hair sprays, gels and mousses
    - i. Polymers used in this venue are referred to as resins
    - ii. Polymer tendency to form films
- c. Characteristics of a good styling resin
    - i. Creates substantive film on the hair so it can be easily washed away
    - ii. Hold hair with flexibility so the hair can move without breaking
    - iii. Be transparent so it does not reduce the hair's natural gloss
    - iv. Does not flake when brushed
    - v. Does not absorb moisture from the atmosphere and become sticky
- d. In general, the higher the molecular weight, the greater the holding power of the resin, but higher molecular weight can also result in higher viscosity, which can have a negative effect on the spray pattern of the hair spray
- e. The glass transition temp also affects how the polymer behaves on hair
    - i. Above the T_g the film will be more flexible
    - ii. Below the T_g the film will harden and become more brittle
- f. Working through the hurdles
    - i. First hairsprays used shellac, which is a resinous material derived from insects
    - ii. Worked to hold hair in place, it also produced a water-insoluble film that was difficult to wash out of the hair
    - iii. Incorporating synthetic polymers into hair styling helped overcome this problem
    - iv. Polyvinylpyrrolidone (PVP) first synthetic used
        1. water-soluble, clear, flexible film
        2. problems: PVP is hygroscopic, so it tends to absorb moisture from air → sticky
    - v. Copolymer resins, polyvinylpyrrolidone vinyl acetate (PVA-VA)
        1. less susceptible to atmospheric moisture

2. hard to remove with shampoo
3. carboxylated resins

vi. Additives
1. plasticizers, isopropyl myristate – make the film more flexible and less brittle
2. neutralizing agents, aminomethyl propanol (AMP) help control film hardness and solubility
3. R&D – create polymers that can be incorporated into formulas that contain water

III. Conditioning Polymers

a. Used in shampoos and conditions to provide slip, detangling and anti-static properties; conditioning polymers can also add body, firmness and texture

b. In skin creams, polymers provide moisturization and humectancy
i. Cationic polymers, proteins or silicones

c. Cationic polymers
i. Widely used in shampoos
ii. Compatible with anionic surfactants (unlike cationic surfactants)
iii. Can form a film that contributes to hair's body and fullness
iv. Rely on a dilution/deposition mechanism
1. when a shampoo with a cationic polymer is applied to hair, it becomes diluted; this causes the concentration of the anionic surfactant to fall below the CMC, which causes the polymer to precipitate and plate out on the hair
2. when the shampoo is rinsed away, some of the polymer remains on the hair because of its insolubility in water and electrostatic interaction
3. when a polymer is in a shampoo formula, it is compatible because it is associated with the anionic surfactant
4. when it is applied to hair, the shampoo is diluted and the association between polymer and surfactant is disturbed
5. when the concentration of surfactant falls below the CMC, the polymer is no longer compatible and it plate out on the hair
6. the amounts of various polymers remaining on the hair after treatment has been investigated
a. the degree of substantivity of a cationic polymer on hair is dependant on the molecular weight of the polymer, alkalinity and salt concentration of the solution it is delivered in (the type of hair is also a factor)

7. the first cationic polymer that introduced conditioning shampoos was a cellulose-based ingredient called polyquaternium 10
    a. it is produced by reacting hydroxyethylcellulose with epichlorhydrin and then quaternized with trimethylamine
    b. since then, a variety of cationic polymers have been introduced

d. Silicones
    i. Polymerization of siloxanes
    ii. Conditioning polymers
        1. dimethicone used in shampoos, conditioners, and skin creams
        2. provides smoothness, lubricity and shine but isn't sticky or oily
        3. in hair it improves combining, shine and mangability
        4. primary ingredient in two-in-one shampoos
    iii. dimethicone can be difficult to incorporate into some formulations
        1. dimethicone derivatives (copolymerizing dimethicone with polyethylene glycol)

e. Proteins
    i. Proteins used in cosmetic formulations for conditioning
        1. first hydrolyzed for solubility purposes
            a. can be used in clear solutions
        2. hydrolyzed collagen is the most widely used example
            a. improves body, gloss, combining and manageability
            b. has been shown to absorb into hair
            c. on skin, hydrolyzed collagen contributes to moisturization
        3. other proteins such as vegetable and milk proteins
            a. alternative to animal by-products

IV. Thickeners
a. Polymers have been used to thicken products
b. They also offer suspension properties
    i. Stabilize emulsions or suspending gelatin beads or pearlizing materials
    ii. Unlike surfactant thickeners, polymeric thickeners are unaffected by pH or salt concentration
    iii. May require less material to thicken
    iv. A product that requires 3.0% of a surfactant thickener, like cocamide DEA, only needs 0.5% of a cellulose polymer for the same result
    v. Cellulose is a polydisperse polymer with a molecular weight of 3,500 to 36,000

1. By itself, cellulose is a water-insoluble material because of its intermolecular hydrogen bonding
2. sugar-based polymer
3. can be converted into a water-insoluble polymer by reacting the hydroxyl groups to produce ethers or esters
4. most used cellulose polymers – hydroxyethylcellulose (HEC), hydroxypropyl methylcellulose (HPMC)

vi. Modified starches also used
1. desirable for skin creams and lotions

vii. polyacrylic acid
1. when neutralized, produces a clear, highly viscous solution
2. good for gels, shampoos

V. Conclusion

a. Polymers used other than to thicken
i. Solubilizers for fragrancing
ii. Reduce irritation toward surfactants
iii. To opacify formulas
iv. Improve cleansing properties
v. Provide humectancy
vi. Water absorption
vii. Delivery
viii. Preservatives

b. Polymer age began around 1900s, just scratched the surface