

Theories or Mechanisms of Adhesion

Should consider:

- 1) Surface science
- 2) Polymer Characteristics
- 3) Interactions between polymers and surfaces

No unifying theory that describes all adhesive bonds!!!

Four mechanisms or theories of Adhesion

1. Mechanical Interlocking
2. Diffusion Theory
3. Adsorption and Surface Reaction
4. Electrostatic

1. Mechanical Interlocking

- 1) Applicable in situations where the adherends are impermeable to the adhesive.
- 2) Surface of adherend is usually rough.
- 3) Interphase may exhibit a “lock and key” effect (Fig 6.7).
- 4) Rubber tire repair kit is a good example.
- 5) Rough surface increases area of physical contact.

Demonstration of surface roughness on adhesion for a copper surface bonded with epoxy adhesive (Arrowsmith Figure 6.8).

Pore penetration by adhesives is dependent on the radius of the pore (Table 6.1).

Table 6.1 Packham's calculation of distance penetrated by molten polystyrene into a microporous surface.

Pore radius (micrometers)	Distance penetrated into "x" (micrometers)
1000	220
10	22
1	7
0.1	2.2
0.01	0.7

2. Diffusion Theory

- 1) Based on the solubility of one material into another.
- 2) *Interphase* instead of an interface (Figure 6.3).
- 3) No stress concentration in the interphase because no discontinuity exists in the physical properties.
- 4) Use cohesive energy density to interpret diffusion bonding.

Cohesive Energy Density (C.E.D.)

$$C.E.D. = \frac{E_{coh}}{V}$$

E_{coh} is the amount of energy necessary to separate molecules to an infinite distance.

V is the molar volume

Solubility Parameter

$$d = \sqrt{\frac{E_{\text{coh}}}{V}}$$

Table 2.5 from *Principles of Polymer Systems*

one criterion for good adhesion: *the adhesive and the adherend should have similar solubility parameters.*

Adhesive bond strength versus solubility parameter (Figure 6.4).

Solvent Welding

- 1) methylene chloride - PMMA
- 2) PVC + plasticizer in THF and toluene - PVC

Block Copolymers at Interfaces

PMMA and PS are not soluble in one another

Block copolymers with varying length of the two blocks were annealed and the level of adhesion increased with the increase of molecular weight of the blocks at any thickness of the block copolymer (Figure 6.5).

Adhesion was controlled by the entanglement molecular weight (M_e) of the block on each side of the interface. When M_e is exceeded for both sides of the interface and bonding is improved the *aerial chain density* (S) has been achieved.

Physics of the separation process are governed by a

phenomenon called *chain pull-out*.

3. Adsorption and Surface Reaction

- 1) Adhesive molecules are attracted to specific sites on the adherend.
- 2) Primary and secondary valance forces.

Acid-base Interactions

Owens and Wendt - Fowkes equation:

$$W_A = 2\sqrt{g_1^d g_2^d} + W_A^{AB}$$

Fowkes - Drago equation:

$$W_A^{AB} = kN^{AB} (E_A E_B + C_A C_B)$$

Where: N^{AB} is the number of acid-base pairs interacting in the interface or interphase.

K is a proportionality constant that corrects for units

E and C are experimentally determined constants

E is electrostatic

C is covalent

Acids attract bases and bases attract acids.

Guttman donor-acceptor numbers

Pearson's Hard-Soft Acid-Base Principle

Covalent Bonding

molecular species are formed by the sharing of electron pairs. These bonds are a primary focus of organic chemistry.

(Bond energy: 35 - 150 kcal/mole)

Importance of having covalent bonding is shown in the following example of the work of adhesion calculation for a 3 component system, and the results shown in Table 6.2.

$$W_A^l = 2\{\sqrt{g_1^d g_l^d} - \sqrt{g_1^p g_l^p} - \sqrt{g_2^d g_l^d} - \sqrt{g_2^p g_l^p} + \sqrt{g_1^d g_2^d} + \sqrt{g_1^p g_2^p}\}$$

Coupling Agents

Coupling agents are materials with two chemical functions, one of which is reactive with the inorganic phase and the other which is reactive with the organic phase.

- 1) Silanes (glass - polyester) (Figure 6.13)
- 2) Titanates (Kevlar - phenolic) (Figure 6.14)
- 3) Chrome complexes (methacrylic acid)

4. Electrostatic Theory

Electrostatic forces occur between atoms or molecules which bear a charge.

- ++ Repulsive**
- Repulsive**
- +- Attractive**

Figure 6.1

Examples

- 1) Amber rod rubbed with fur
- 2) Rubber balloon rubbed acquires a surface charge and sticks to non conductive surfaces.
- 3) Bees attracting pollen
- 4) Light emitted in breakage of bonds
- 5) Tape applied to an AM transistor radio: pull-off creates static.

Electrostatic adhesion is used extensively in the coatings industry.

Polymer particles are negatively charged and the piece to be coated is positively charged or grounded.

Criteria for obtaining a good adhesive bond

- 1) Choose an adhesive which is soluble in the adhrend
- 2) Choose an adhesive that spontaneously wets the surface.
- 3) Make sure that the surface has microscopic roughness
- 4) Eliminate weak boundary layers
- 5) Choose an adhesive with the right viscosity/cure relationship
- 6) For adverse environments, provide covalent bonding.