CHAPTER 10

Characteristics of the Surfaces of Biomaterials

10.1 SURFACE CHARACTERISTICS RELATED TO CHEMICAL BONDING

The surface of a material has different chemical bond characteristics from the bulk and, therefore, should be considered to be different.

10.1.1 Polar Groups

Molecules in which one atom has an excess of negative charge, i.e., unequal sharing of bonding electrons. One atom is more electronegative than the others.

1) Can become ionized and interact by ionic forces (10-20 kcal/mol.). Like ionic charges repel.
2) Form permanent dipoles and interact by:
   a. Hydrogen bonding (approx. 3-7 kcal/mol)
   b. Molecular orientation
   c. Induction interactions
3) Intensity of dipole/dipole interactions are dependent on distance of separation and orientation of individual dipoles. Parallel dipoles can repel each other.
4) Polar/ionic groups can have acidic (proton donating or electron accepting) or base (proton accepting, or OH or electron donating) character. Acid-base interactions are likely as opposed to acid-acid or base-base which are repulsive.
5) Biomaterials with ionic groups or strong dipoles on the solid surface will tend to bind water molecules (hydrophilic).
6) The presence of specific polar groups is inferred from determination of elements, molecules, and bonding in the surface of biomaterials.

10.1.2 Nonpolar (Apolar) Molecules

Nonpolar molecules might be available to undergo van der Waals interactions (nonspecific) with biological molecules. The "bond energy" of approximately 1-2 kcal/mol. is due to the correlation of the electronic motion of the molecules.

10.1.3 Surface Free Energy (Critical Surface Tension)

1) An atom in the free surface has no neighbors on one side. Since bond energies are negative its energy is higher than interior atoms by the missing share of bond energy.
2) Chemical bonds of surface atoms are asymmetrically directed toward the interior of the material, attracting the surface atoms inward and causing surface tension.
3) Energy required to create a free surface (e.g., by fracture of the material) is reflected in the surface energy. Thermodynamic forces act to minimize surface energy.
   a. Low energy molecules near the surface are translated and rotated toward the surface. Low energy components in the bulk migrate (diffuse) to the surface.
      These include:
      1. Low molecular weight additives (e.g., antioxidants, processing aids, etc.) or degradation products
      2. Contaminants
   b. Exposed surface groups attempt to lower their energy (i.e., unsatisfied bonding) by adsorbing or reacting with ambient molecules.
      1. Adsorption of hydrocarbon (contamination) by all materials

2. Oxide formation on metals

4) Surfaces with low critical surface tension are hydrophobic. Hydrophobic surfaces interrupt the hydrogen bonded structure of water (i.e., force water molecules to structure in an ice-like conformation on or near the surface). Water droplets do not spread on hydrophobic surfaces.
5) "Bond energy" of hydrophobic interactions (dispersion force) is approx. 1-2 kcal/mol.
6) Critical surface tension of solids can be determined from contact angle measurements and the Zisman plot.

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10.2 SURFACE CHEMISTRY RELATED TO BONDING OF BIOLOGICAL MOLECULES

10.2.1 Molecules

10.2.1.1 Type (with respect to polarity)

1) Magnitude of the dipole moment. Molecules with no dipole moment are nonpolar and thus provide a very hydrophobic surface (e.g., PTFE).
2) Potential to become ionized to form ionic bond.

10.2.1.2 Distribution

Could affect chemical specificity by providing a certain template of bonds.

10.2.1.3 Density

For example, hydrogels have a very low density of molecules at the surface to accommodate a considerable amount of water.

10.2.1.4 Mobility

Surface of certain polymers (e.g., polyurethanes) are dynamic (i.e., always changing because of mobility of the molecules).

10.2.2 Surface Characteristics Resulting from Chemistry

10.2.2.1 Hydrophobicity

10.2.2.2 Charge

10.3 POROSITY (Pore characteristics and what features that they affect)

Void Fraction; Percentage Porosity

Strength of the material
Amount of tissue that can form in the material
Surface area

Pore Diameter; Interconnecting Pore Diameter

Surface area
Size of the tissue elements (*e.g.*, cells) that can infiltrate the material

Pore Orientation

Direction of cell migration and architecture of the tissue that forms

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10.4 FACTORS AFFECTING THE BIOMATERIAL SURFACE

1) Exposure to air (e.g., hydrocarbon contaminants).

2) Handling (e.g., contamination with particles and alteration of topography).

3) Storage time (e.g., residual stresses can result in dimensional changes).

4) Sterilization

   a. Autoclave (steam)
      Effects of temperature and absorbed water in altering mechanical properties of certain thermoplastics.

   b. Dry heat (prolonged high temperatures)

   c. Gas (ethylene oxide)
      Prolonged period of aeration required for certain polymers.

   d. Gamma radiation
      Chain scission followed by oxidation.
      Crosslinking of certain polymers.

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10.5 SURFACE CHARACTERISTICS AND METHODS OF ANALYSIS

Scale of Features (Not Detection Depth of Penetration)	Characteristics	Method
Macroscopic (>10 μm)	Hydrophobicity	Contact angle (Critical surface tension from Zisman plot)
	Charge	Electrophoresis of particles (zeta potential)
	Topography	Light microscopy (LM) Scanning electron microscopy (SEM)
	Porosity	LM, SEM, Mercury intrusion porosimetry
	Water content	Drying/weighing
	Surface area	Gas adsorption methods
	Mechanical compliance	Mechanical testing (modulus of elasticity)
Microstructure		
(>0.2μm)	Particles on surface	Light microscopy/SEM
	Topography Profilometry (stylus pulled	Light microscopy, SEM, over surface)
	Crystallite Structure/Size	X-ray diffraction

Nanostructure

>0.01μm (>10 nm)	Particles	SEM
	Topography	SEM, Profilometry
1-10 nm	Elemental composition analysis (EDX)	Energy dispersive x-ray
		Wavelength dispersive x-ray analysis (WDX)
		Electron spectroscopy for chemical analysis (ESCA, also referred to as x-ray photoelectron spectroscopy, XPS)
		Auger electron spectroscopy (AES)
		Secondary ion mass spectroscopy (SIMS)
	Molecules/Bonding (including depth profile, DP)	ESCA (DP)
		AES (DP)
		SIMS (DP)
		Infrared Spectroscopy (IR)
	Crystal structure	X-ray diffraction (XRD)

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10.6 BIOADHESION (TISSUE BONDING): PHYSICAL AND CHEMICAL MECHANISMS

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1. Physical/Mechanical
   a. Entanglement of macromolecules (nm scale)
   b. Interdigitation of ECM with surface irregularities/porosity (μm scale)

2. Chemical
   a. Primary
      ionic

   b. Secondary
      1) hydrogen bonding
      2) van der Waals

   c. Hydrophobic Interactions

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10.7 SIZE AND TIME SCALES FOR BIOADHESION

Size Scale	Tissue Level	Mechanism of Bonding	Time Constant	Measurement(s)
mm-cm	Organ	Interference Fit Grouting Agent Tissue (Bone) Ingrowth Chemical Bonding	Weeks-Months-Years	Radiographic (qualitative) Mechanical Testing (quantitative)
mm	Tissue	Same	Weeks	Mechanical Testing Light Microscopy/Histology (qualitative) Scanning Electron Microscopy (qualitative and quantitative)
µm	Cell	Integrin	Days-Weeks	Histology Transmission Electron Microscopy (qual.)
nm	Protein GAG	Secondary Bonding Hydrophobic Interactions	Seconds-Minutes-Hours-Days	Immunohistochemisty (qual.) Adsorption Isotherm (quan.)
nm	Mineral crystallites	Epitaxy Ionic Bonding	Seconds-Minutes-Hours-Days	Transmission Electron Microscopy *In vitro* Precipitation (quan.)

10.8 CHEMICAL AND PHYSICAL* BONDING (Nanometer Scale)

Biomaterial			Across Interface	Biological Molecules	
Classification	Bulk	Surface 0.1-5 nm		Intermolecular	Intramolecular
Metals.....	Metallic	Ionic	Hydrogen (3-7 kcal/mol)	Covalent	Covalent
Ceramics.....	Ionic/ Covalent	Ionic	van der Waals (1-2)	Ionic	Ionic
Polymers		CE	Ionic** (10-20)		Hydrogen
- Intramol.....	Covalent				
.....	Ionic				
		Water (Hydrogel)	CE		Van der Waals
- Intermol.....	Covalent		Hydrophobic interactions (1-2)		Hydrophobic interactions
.....	Ionic				
.....	CE				

*Physical bonding - chain entanglement (CE), i.e., entanglement of polymer chains with biological macromolecules.

**Includes epitaxial crystal growth of biological mineral (e.g., bone mineral, apatite) on the biomaterial (e.g., synthetic hydroxyapatite or certain metal oxides).