

**3.051J/20.340J Problem Set 1**  
**due 2/16/06**

1. (12 pts) Bone tissue engineering generally involves the implantation of a synthetic or biologically derived material that upon implantation allows for bone in-growth and eventual replacement. In a recent publication, De Groot and coworkers (*Tissue Eng.* **2003**, 9, 535) compared the structures of 3 commercially produced biphasic calcium phosphate (BCP) porous scaffolds for bone tissue engineering. BCP is a two phase material of hydroxyapatite and tricalcium phosphate. SEM images below illustrate cross-sections of the scaffolds manufactured by Zimmer (left image), Dytech (middle image) and IsoTis (right image). Scale bar is 1 mm.

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See Fig. 3, top images, in Li, Shihong, Joost de Wijn, Jiaping Li, Pierre Layrolle, and Klaas de Groot. "Macroporous Biphasic Calcium Phosphate Scaffold with High Permeability/Porosity Ratio." *Tissue Eng* 9 (2003): 535-548.

- a) What aspects of the primary chemical structure, higher order (meso) structure and/or microstructure make these scaffolds useful for bone tissue engineering?
- b) Download the article by De Groot and coworkers through the MIT library. What processing approaches resulted in the dramatically different pore morphologies observed in the SEM images for the 3 BCP scaffolds?
- c) A table of the scaffold porosities and specific permeabilities measured by De Groot and coworkers is provided below. Explain why the IsoTis scaffold, with the lowest porosity, exhibits the highest permeability.

| Manufacturer | Specific permeability (m <sup>2</sup> ) | Porosity (%) |
|--------------|---|--------------|
| Zimmer       | $0.02 \times 10^{-9}$                   | 75           |
| Dytech       | $0.12 \times 10^{-9}$                   | 80           |
| IsoTis       | $0.34 \times 10^{-9}$                   | 60           |

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2) (16 pts) Recently, Yokoyama and coworkers described the preparation of protein-resistant surfaces on polystyrene (PS) through the addition of 10% of a block copolymer additive (PS-*b*-PME3MA) whose structure is shown below (A. Oyane et al., *Adv. Mater.* **2005**, *17*, 2329; H. Yokoyama et al., *Macromol.* **2005**, *38*, 5180). Contact angle measurements performed on annealed blends with different block copolymer contents are also shown.

a) Explain why the advancing contact angle first decreases then plateaus as the block copolymer content in the blend is increased.

b) What possible energetic driving forces might lead to the phenomenon in (a)?

c) Based on the contact angle data, approximate the composition of the surface for 10 wt% bulk concentration of PS-*b*-PME3MA.

d) For blend systems with >20% block copolymer, what is the molecular origin of the large hysteresis in the contact angle (i.e., the much lower receding contact angle value compared with the advancing angle)?

e) How might the contact angle results change if the terminal group of the methacrylate side chain were changed to a hydroxyl (-OH)?

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Please see Scheme 1 and Fig. 9 in Yokoyama, H., T. Miyamae, S. Han, T. Ishizone, K. Tanaka, A. Takahara, and N. Torikai. "Spontaneously Formed Hydrophilic Surfaces by Segregation of Block Copolymers with Water-Soluble Blocks." *Macromolecules* **38** (2005): 5180-5189.

3) (12 pts) Chen et al. investigated adhesion of endothelial cells on titanium oxide coatings as a possible surface treatment to reduce thrombogenesis on arterial stents. (*Surface & Coatings Tech.* **2004**, *186*, 270). X-ray diffraction measurements revealed the as-prepared coatings to be amorphous, while coatings heat-treated for 0.5 hours at 700 °C were crystalline. Contact angle measurements were made utilizing different liquids to

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determine values for the polar and disperse components of the surface energy, as listed in the table below.

- a) Can the work of cohesion for titanium dioxide be estimated from the measurements of Chen et al.? Explain.
- b) What chemical groups might you expect to observe on the TiO<sub>2</sub> surface?
- c) Why is the measured surface energy of the titanium oxide coating lower after heat treatment?
- d) Based on the surface energies provided, calculate the work of adhesion between the surface and water for the amorphous and crystalline coatings? How might this influence protein adsorption?

| material                   | $\gamma_p$ (dyn/cm) | $\gamma_d$ (dyn/cm) | $\gamma$ (dyn/cm) |
|----------------------------|---------------------|---------------------|-------------------|
| amorphous titanium oxide   | 30                  | 29                  | 59                |
| crystalline titanium oxide | 14                  | 26                  | 40                |
| water                      | 51                  | 22                  | 73                |