

3.051J/20.340J Problem Set 2
due 2/28/06

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1. (21 pts) CoCrMo alloys form a passivating oxide on their surface that renders them useful for orthopaedic implants. Such implants remain susceptible, however, to fretting corrosion, which occurs as a consequence of repetitive rubbing of the implant against a second hard surface (e.g., another implant component or bone). To study fretting corrosion, Contu et al. (*Corrosion Sci.* **2005**, *47*, 1863) employed a tribo-electrochemical cell, illustrated below, employing a CoCrMo alloy (66:28:6 wt ratio Co:Cr:Mo) as the working electrode, Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode (SCE is +0.231V on the standard hydrogen electrode (SHE) scale.) A ceramic tube in contact with the sample was rotated periodically to create a rubbing action on the surface. Dissolved oxygen was removed from electrolyte solutions by bubbling with argon gas for 24 h prior to the experiments. The figure below shows data for the open circuit potential (OCP) measured before, during and after 3 rotations of the ceramic tube in buffered solutions at pH 4 (solid) and pH 7 (dashed).

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See Fig. 1 and Fig. 2(a) in Contu, F., B. Elsener, and H. Böhni. "Corrosion Behaviour of CoCrMo Implant Alloy During Fretting in Bovine Serum." *Corrosion Science* 47 (2005): 1863-1875.

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- a) Why does the OCP first drop rapidly then rise rapidly and plateau following each abrasion of the alloy surface by the ceramic tube?
- b) Write the expected anodic half-reaction(s) for this alloy at pH 4. Based on this reaction and the Nernst equation, provide an expression for the measured electrical potential across the rubbed alloy surface.
- c) What is the expected cathodic half reaction at pH 4 and pH 7 for this experiment?
- d) Why is the OCP measured at pH 4 higher than the value measured at pH 7?
- e) Why does the open-circuit potential after rubbing plateau to a different value than the original measured OCP for this alloy?
- f) The figure below provides data from cathodic polarization (increase in the cathodic reaction relative to anodic reaction) experiments at pH 4 for the CoCrMo alloy in electrolyte solution (phosphate buffer) vs. serum. Shown is the measured current density as a function of the potential. Provide an explanation for the reduced current measured in serum compared to buffer. Would this be a favorable or unfavorable effect *in vivo*?

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See Fig. 4(a) in Contu, F., B. Elsener, and H. Böhni. "Corrosion Behaviour of CoCrMo Implant Alloy During Fretting in Bovine Serum." *Corrosion Science* 47 (2005): 1863-1875.

2. (19 pts) Catalase is an enzyme (mol. wt.: 247kDa, diameter: 10.5 nm) found in liver cells that catalyses the conversion of hydrogen peroxide to water and oxygen. Its catalytic activity is of interest for biosensor applications. As an approach for fractionating catalase from biological solutions, Jia and coworkers (*Int. J. of Biol. Macromol.* **2005**, 37, 42) prepared chitosan microspheres coated with a covalently attached dye, Cibacron Blue F3GA, which exhibits strong binding to catalase. The figure below shows an SEM image of the chitosan particles. The wet density of the spheres was found to be 1.328 g/mL. Adsorption studies were performed to determine the amount of

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catalase adsorbed to the particles as a function of solution concentration. An adsorption isotherm for pH 7 is shown below.

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See Fig. 1 and 4 in Shentu, Jingling, Jianmin Wu, Weihua Song, and Zhishen Jia. "Chitosan Microspheres as Immobilized Dye Affinity Support for Catalase Adsorption." *International Journal of Biological Macromolecules* 37 (2005): 42-46.

- a) Assuming a Langmuir model, determine the affinity constant K_a and the maximum surface coverage Γ_{\max} for CAT adsorption on the dye-linked chitosan beads.
- b) From the obtained value for Γ_{\max} , calculate the effective area per protein, stating any assumptions you make.
- c) How does your value compare to the expected molecular area for catalase, given the protein dimensions? Explain the possible origin of discrepancies.
- d) At pH 7, both CAT and the dye Cibacron Blue F3GA have a net negative charge. Explain why CAT adsorption onto the chitosan particles still occurs.
- e) The data below shows the amount of adsorbed CAT as a function of ionic strength of the solution (increasing NaCl content). Explain why a decrease in adsorption is observed with increasing salt content in solution.

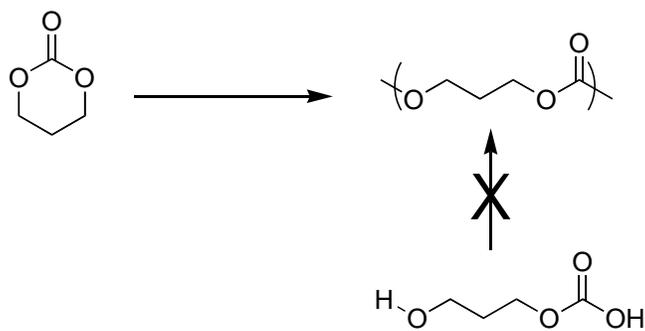
Images removed for copyright reasons.

See Fig. 3 in Shentu, Jingling, Jianmin Wu, Weihua Song, and Zhishen Jia. "Chitosan Microspheres as Immobilized Dye Affinity Support for Catalase Adsorption." *International Journal of Biological Macromolecules* 37 (2005): 42-46.

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3) (10 pts) Aliphatic polycarbonates have been gaining much attention as degradable polymers, due to biocompatibility or bioresorbability, while aromatic polycarbonates are hardly hydrolysable. Feijin and coworkers have reported *in vitro* and *in vivo* degradation of poly(trimethylene carbonate) (PTMC), an aliphatic polycarbonate with a glass transition temperature of $T_g = -15^\circ\text{C}$, and found interesting aspects of its degradation (*Biomaterials*, 2006, 27, 1741).

a) PTMC is synthesized by ring-opening polymerization of 1,3-dioxan-2-one rather than by polycondensation of carbonic acid mono-(3-hydroxy-propyl)ester, as shown in the scheme below. Why?



Synthetic scheme of PTMC

b) Various PTMCs were implanted in the femur and tibia of rabbits. Mass losses and molecular weight (MW) changes were monitored as a function of time. Here, x of PTMC_x stands for MW (kDa) of TMC. As can be seen in Figs 1 and 2, in the initial degradation stage, the mass of the polymeric materials decreased with time; however, MW values did not change significantly. Explain what happened.

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See Fig. 1 and 2 in Zhang, Zheng, Roel Kuijer, Sjoerd K. Bulstra, Dirk W. Grijpma, and Jan Feijen. "The In vivo and In vitro Degradation Behavior of Poly(trimethylene carbonate)." *Biomaterials* 27 (2006): 1741-1748.

c) Table 2 shows water contact angles of PTMC surfaces. The results indicate that low MW PTMC became more hydrophilic than high MW PTMC after conditioning in water

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for 1 week at 37°C, while both polymer surfaces presented similar wetting properties before conditioning. What is a likely explanation for these results?

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See Table 2 in Zhang, Zheng, Roel Kuijer, Sjoerd K. Bulstra, Dirk W. Grijpma, and Jan Feijen.

"The In vivo and In vitro Degradation Behavior of Poly(trimethylene carbonate)." *Biomaterials* 27 (2006): 1741-1748.

d) Mass losses of PTMCs in lipase solution is shown in Figure 3. Mass loss rate of high MW PMTC was larger than that of low MW PMTC. These *in vitro* results were compared with the *in vivo* results (Fig. 1 above). In general, hydrolysis of high MW polymers is slower than for low MW polymers because high MW polymer surfaces are more hydrophobic, making H⁺ and/or OH⁻ ion less accessible to the surface. In this study, high MW PTMC presented a more hydrophobic surface after conditioning, as shown in Table 2. What is a plausible reason for the increased degradation of high MW PMTC in the presence of lipase?

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See Fig. 3 in Zhang, Zheng, Roel Kuijer, Sjoerd K. Bulstra, Dirk W. Grijpma, and Jan Feijen.

"The In vivo and In vitro Degradation Behavior of Poly(trimethylene carbonate)." *Biomaterials* 27 (2006): 1741-1748.