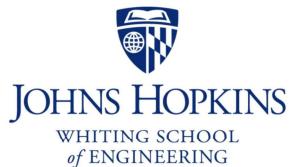


Final

Wednesday, May 5, 2021 9:01 AM



Department of Materials Science and Engineering

EN. 510.316 Biomaterials I

Spring 2021 | Final Exam

5/5/2021 9:00 a.m. – 12:00 noon

Name: _____

1 (30')	2 (25')	3 (15')	4 (20')	5 (10')	6 (20')	7–8 (10')	Total (120' + 10')

Instructions:

- This is an open-book exam. Answer all questions in Q1–Q6. Q7 and Q8 are bonus questions (optional).
- You should work on this exam independently. No consultation or discussion is allowed!
- If you do not have a printer, write the answers to Q1 on a separate sheet of paper neatly. Mark your answers to each question neatly. For example, 1.1. A; 1.2. B; 1.3. C 1.4. D, etc. Write answers to Q2 to Q8 on separate sheets of papers. Turn all answer sheets in on the BlackBoard.

1. Multiple Choices. Choose ONE correct answer to each of the following question, and enter the answers to the following scantron. (30' total, 2' per question)

Use pencil or pen to fill the selected circle completely.

INSTRUCTIONS: []

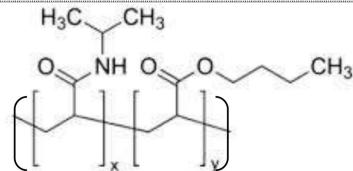
Example: A B C

SECTION 1 _____

1 A <input type="radio"/> B <input type="radio"/> C <input type="radio"/> D <input type="radio"/>	6 A <input type="radio"/> B <input type="radio"/> C <input type="radio"/> D <input type="radio"/>	11 A <input type="radio"/> B <input type="radio"/> C <input type="radio"/> D <input type="radio"/>
2 A <input type="radio"/> B <input type="radio"/> C <input type="radio"/> D <input type="radio"/>	7 A <input type="radio"/> B <input type="radio"/> C <input type="radio"/> D <input type="radio"/>	12 A <input type="radio"/> B <input type="radio"/> C <input type="radio"/> D <input type="radio"/>
3 A <input type="radio"/> B <input type="radio"/> C <input type="radio"/> D <input type="radio"/>	8 A <input type="radio"/> B <input type="radio"/> C <input type="radio"/> D <input type="radio"/>	13 A <input type="radio"/> B <input type="radio"/> C <input type="radio"/> D <input type="radio"/>
4 A <input type="radio"/> B <input type="radio"/> C <input type="radio"/> D <input type="radio"/>	9 A <input type="radio"/> B <input type="radio"/> C <input type="radio"/> D <input type="radio"/>	14 A <input type="radio"/> B <input type="radio"/> C <input type="radio"/> D <input type="radio"/>
5 A <input type="radio"/> B <input type="radio"/> C <input type="radio"/> D <input type="radio"/>	10 A <input type="radio"/> B <input type="radio"/> C <input type="radio"/> D <input type="radio"/>	15 A <input type="radio"/> B <input type="radio"/> C <input type="radio"/> D <input type="radio"/>

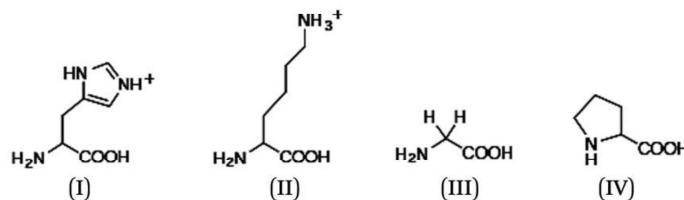
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- 1.1 The polymer shown to the right is a random copolymer of (N-isopropylacrylamide) (poly(NIPAAm)) and butyl acrylate (BA) with monomer fractions of x and y , respectively. Which of the following is **TRUE**?



- (a). The LCST of the copolymer is higher than that of poly(NIPAAm), when $x/y = 3$;
- (b). The LCST of the copolymer increases as y increases;
- (c). The amount of primary bound water increases as y increases;
- (d). The amount of secondary bound water decreases when the temperature increases over LCST, when $x/y = 3$.

- 1.2 Which of the following amino acids is/are most frequently found in desmosine and isodesmosine crosslinks in native extracellular matrix protein materials?



- (a). Amino acid residue (II)
- (c). Amino acid residues (III)
- (b). Amino acid residues (II) and (III)
- (d). Amino acid residues (III) and (IV)

- 1.3 Collagen Type I exhibits hierarchical structures with multiple levels of complexity and order. Which of the following statements is **TRUE** about the structure of collagen Type I?

- (a). Five amino acid residues are found in each turn of the α -helix in the collagen chain.
- (b). Three individual collagen protein chains assemble into a β -sheet structure.
- (c). Intra-chain hydrogen bonds are primarily responsible for the formation and stabilization of the α -helical conformation of each collagen chain.
- (d). Collagen chains assemble into fibrils that are stabilized by inter-chain hydrophobic interactions.

- 1.4 You are tasked to develop a medical adhesive to bond a new biodegradable nerve wrap together between the two polymer surfaces (to the right, the arrow shows where the adhesive is applied). The two sides (surfaces) of the wrap have critical surface tensions of 85 and 60 dynes/cm, respectively. Assuming that the surfaces are smooth without textures, which of the following criteria would be most important for your design?



- (a). This new adhesive should have a surface tension (γ_{LV}) higher than 85 dynes/cm;
- (b). This new adhesive should have a surface tension (γ_{LV}) between 85 and 60 dynes/cm;
- (c). This new adhesive should have a surface tension (γ_{LV}) lower than 60 dynes/cm;
- (d). The surface tension (γ_{LV}) of the adhesive is irrelevant, as the two wrap surfaces could bond with each other.

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- 1.5 Which of the following best describes structures of **both** Type I collagen **and** elastin?

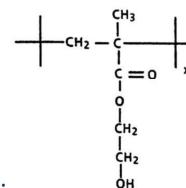
- (a) Both structures are stabilized by physical crosslinks *via* β -pleated sheets;
- (b) Both structures are stabilized by chemical crosslinks *via* β -pleated sheets;
- (c) Both structures have polypeptide chains assembled into α -helical structures.
- (d) Both structures are stabilized by chemical crosslinks involving lysine residues.

- 1.6 Compare two poly(hydroxyethyl methacrylate) (to the right) sheets:

"Sample A" has been exposed to air for 2 days, and
 "Sample B" has been submerged in pure water for 2 days.

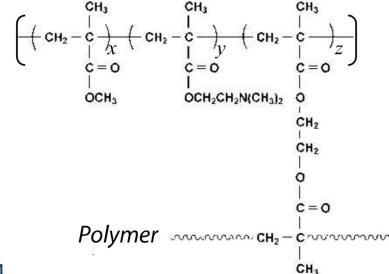
Which of the following is **TRUE**?

- (a). The water contact angle of Sample A is lower than that of Sample B;
- (b). The critical surface tension of Sample A is lower than that of Sample B;
- (c). The surface oxygen content of Sample A is higher than that of Sample B;
- (d). The surface energy of Sample A *in air* is higher than that of Sample B.

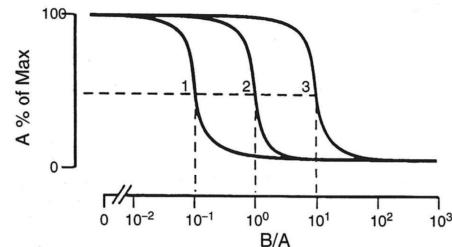


- 1.7 Consider the following crosslinked random copolymer (shown to the right) in water. The molar fractions of the first, second and third units in the backbone of this copolymer are represented as x , y , and z .
 Which of the following statement is **TRUE**?

- (a). The swelling ratio of this hydrogel increases if the fraction of the first unit (x) increases at pH 4.
- (b). The swelling ratio of this hydrogel increases if the fraction of the second unit (y) increases at pH 4.
- (c). The swelling ratio of this hydrogel increases if the fraction of the third unit (z) increases at pH 4.
- (d). The swelling ratio of this hydrogel increases as the solution pH decreases from 4 to 10.



- 1.8 The figure to the right shows the competitive adsorption of Proteins A and B from a mixture at different relative concentrations ($[B]/[A]$) on three different surfaces, 1, 2, and 3. Given that the curves were obtained at ambient temperature and pressure, which of the following is **TRUE**?



- (a). On Surface 3, you will always find more Protein A than Protein B, because Protein A has a higher surface activity than Protein B.
- (b). On Surface 3, you will always find the same ratio of Protein A to Protein B on the surface as that in the solution.
- (c). Protein A has a higher surface activity than Protein B on Surface 3.
- (d). Protein A has a higher surface activity than Protein B on Surface 1.

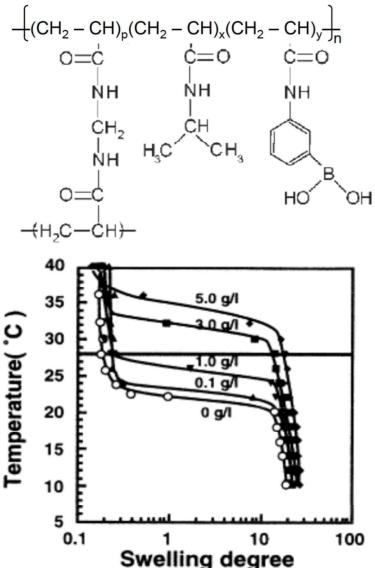
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1.9 Which of the following polysaccharide is an alternating copolymer?

- (a). Hyaluronic acid; (b). Chitin
 (c). Alginate; (d). Chitosan

1.10 Shown to the right is the structure of a temperature- and glucose-sensitive hydrogel (upper panel) and the swelling behavior of the hydrogel in response to temperature at different glucose concentration (in 0 to 5.0 g/L as labelled in the lower panel). Which of the following statements is **TRUE**?

- (a) Increasing the concentration of glucose in the solution will lower the LCST of the hydrogel.
 (b) Increasing fraction p will increase the swelling ratio of the hydrogel.
 (c) Increasing fraction y will increase the LCST in the absence of glucose.
 (d) Increasing the concentration of glucose in the system (when the hydrogel composition is fixed) will increase the density of negative charges in the hydrogel.



1.11 Which of the following is FALSE about the natural silk fiber?

- (a) The secondary structure of silk material is comprised of stacked, anti-parallel β -sheets;
 (b) The silk fibroin protein has an analogous structure to a semicrystalline, thermoplastic polymer;
 (c) Extensive covalent crosslinking of lysine residues in silk fibroin contributes to the high strength and high toughness;
 (d) The silk fibroin solution was extruded in the silkworm duct through a set of orifices, forming fibers with a high degree of alignment.

1.12 A Ph.D. candidate Polly Ester needs to print a biodegradable scaffold for her tissue engineering study. Which of the following approaches that you would NOT recommend her to use?

- (a) Inkjet bioprinting which deposits modified collagen solution droplets in a non-contact manner, which will be crosslinked "instantaneously" thus generating a scaffold;
 (b) A biodegradable polymer powder bed and inkjet head that delivers liquid ink as an adhesive to bond the powder into a solid structure (after the liquid link evaporates);
 (c) Direct ink writing print head which deposits a pre-formed hydrogel into a desired shape and then uses thermal degradation for high resolution;
 (d) Stereolithography which uses light with photons to crosslink a polymer solution in a resin reservoir layer-by-layer.

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1.13	Prof. Crosslincoln is preparing a lecture on piezoelectric materials. Which statement should NOT be included in the presentation (i.e., it is an inaccurate statement)? (a) All piezoelectric materials are ferroelectric, but not vice versa; (b) Piezoelectric materials will produce electric charge (or charge polarization) under mechanical stress; (c) The piezoelectric effect can be either stress-driven or strain-driven; (d) Piezoelectric materials have non-centrosymmetric structure.
1.14	Prof. Crosslincoln asked a student Ella Stomer to create a lotus leaf-inspired superhydrophobic surface for a project. Which of the following characteristics should Ella incorporate into her design? (a) A low water contact angle so water is less likely to spread across the surface; (b) A rough surface with hierarchical features at micro- and nano-scales generated by electrospraying, which minimizes the surface contact with water; (c) A wavy surface feature produced by mechanical sanding to increase surface energy, so water can easily slide off of the surface; (d) A polymer with a surface composition having lower amount of oxygen, so that the surface is less wettable.
1.15	Which of the following strategies can BEST describe an improvement to cyanoacrylate-based surgical superglue? (a) Accelerate the polymerization rate via an anionic chain growth mechanism trigger by the negative charges on red blood cells to cure the adhesive on a wounded tissue; (b) Reduce the degradation rate in tissue following polymerization by adding an enzyme inhibitor; (c) Increase the bonding strength by increasing calcium ion concentration; (d) Increase biocompatibility and reduce inflammatory response by extending the side chain length of the cyanoacrylate.

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2. Natural Polymers: Polysaccharides and Hydrogels

Two different hydrogels can be prepared from sodium alginate (a segment of the alginate structure is shown below) as follows: Gel A is prepared by adding 3% of CaCl_2 solution to 5% sodium alginate solution; and Gel B is prepared by reacting 5% sodium alginate solution with 0.1 M of butylene diamine (BDA) solution ($\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{NH}_2$) in the presence of 1-ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride (EDC) as a catalyst, forming amide bonds between the carboxylic groups in alginate and amino groups in BDA. (25')

- (a). Write the structure of alginate and name the two monomer units forming alginate polymer. Circle the units that directly involved in forming ionic crosslinks with divalent cations.

- (b). Compare the major differences between Gel A and Gel B in terms of crosslinking mechanism, hydrogel stability, and mechanical properties.

Properties	Gel A	Gel B
Crosslinking mechanism (covalent vs. non-covalent; physical vs. chemical crosslinks)		
Hydrogel stability (reversible vs. irreversible; what condition will change the hydrogel crosslinking structure?)		
Mechanical property (List two parameters that can be tuned to vary the modulus of the hydrogel; and how they change)		

- (c). Gel A has been widely used as a material for microencapsulation of islet cells as a potential treatment of diabetes. Describe a setup and steps for the encapsulation process, use a sketch to aid the discussion.

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(d). Name 3 important features for this cell microencapsulation system and briefly explain the ideal design profile (target product profile). Briefly explain the advantages and disadvantages of using alginate hydrogel system.

(e). Barium chloride has also been used instead of calcium chloride to form hydrogel microcapsules with sodium alginate (**Gel A'**). Discuss how and why the capsule permeability and mechanical property of barium alginate hydrogel capsules may be different from calcium alginate capsules.

(f). Describe the method to strengthen the mechanical property of the capsules using poly(L-lysine) (PLL). Give the structure of PLL and briefly justify the choice of PLL for this approach.

(g). The PLL-coated capsules elicit poor biocompatibility as a result of severe adsorption of negatively charged proteins found in serum and physiological media. Propose a method to address this challenge and briefly explain.

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3. Nature Biomaterials: Elastin and Silk Protein

(15')

- (a). Compare the differences in crosslinking structure and morphology of these two protein materials.

Properties	Elastin	Silk protein
Crosslinking structure		
Morphology and chain conformation (crystalline vs. amorphous; alignment degree)		

- (b). Sketch out
- representative**
- stress-strain curves for elastin and silk protein (put two curves on the sample plot), and briefly comment on the difference in terms of general strength, modulus and toughness between the two protein materials.

- (c). Elastin exhibits entropic elasticity. Identify and briefly explain the structural characteristics that contribute to its entropic elasticity.

- (d). Propose a method for generating an artificial elastin material, and briefly explain how you plan to modulate the strength and toughness of the material.

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4. **Surface Energetics.** Consider the adsorption characteristics of serum proteins on a pristine (unmodified) polystyrene (PSt) surface. (20')
- (a) Name the major driving force for surface adsorption of serum proteins on pristine PSt.

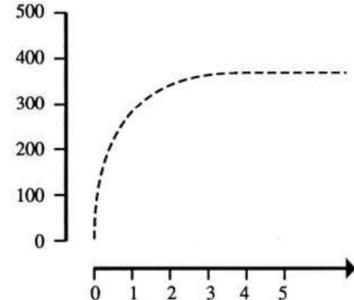
- (b) Consider conducting the surface adsorption experiment at constant temperature and pressure on the pristine PSt surface. State how protein structural parameters and PSt surface characteristics influence the amount of protein adsorbed on polymer surface.

Protein structural parameters:

PSt surface parameters:

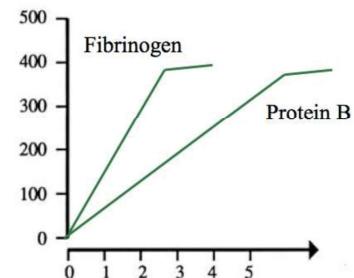
- (c) The figure to the right illustrates the adsorption isotherm of fibrinogen on the pristine PSt surface at room temperature and ambient pressure. Complete the figure by **labeling the axes and units.**

Discuss what key conclusion(s) you can draw from this experiment.



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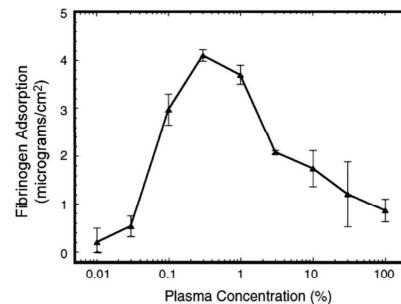
- (d) The figure to the right illustrates the **adsorption kinetics** of fibrinogen at a fixed concentration on pristine PSt surface at room temperature and ambient pressure. Complete the graph by identifying the axes and units. Discuss what key conclusion(s) you can draw from the relationship shown in the figure here.



The same experiment was performed for Protein B with similar charge characteristics, at the same solution (bulk) concentration, with results shown on the same graph above. From this graph, we can

conclude that Protein B has a _____ (higher or lower) molecular size than fibrinogen?

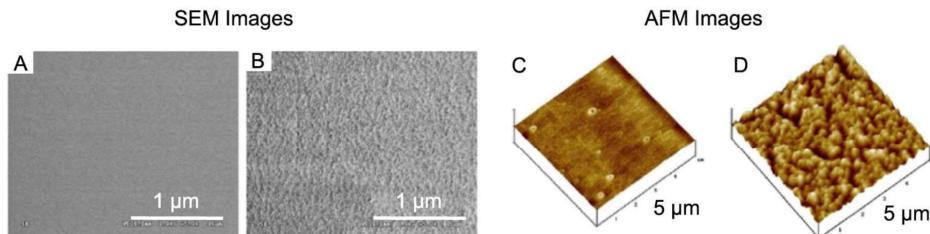
- (e). The figure to the right describes the Vroman effect: the adsorption of fibrinogen on the pristine PSt surface using serum plasma samples with different concentrations. Briefly explain the characteristic of the curve.



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5. Surface Analysis Techniques

Assume the figures below show the SEM (A, B) and AFM (C, D) images of untreated control (A, C) surface and oxygen plasma-treated (50 W, 10 min) surface (B, D) of polystyrene film using glow discharge oxygen plasma (radio frequency of 13.56 MHz). (10')



(a). Give the full names for these two techniques.

SEM: _____;

AFM: _____.

(b). Compare the advantages and disadvantages of the two methods in terms of testing conditions, sample requirements, resolution, cost, and analysis time (on the next page).

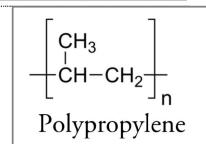
Please fill in the table on the next page.

Parameters	SEM	AFM
Resolution		
Testing condition requirements		
Sample preparation requirements		
Analysis time		

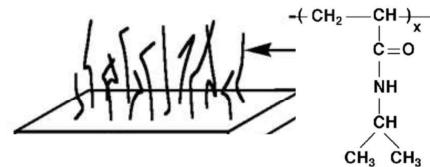
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6. Thermal Sensitive Polymer and Surface Engineering

Consider grafting poly(N-isopropylpolyacrylamide) [poly(NIPAAm)] onto the surface of polypropylene (PP) through free radical mediated chain growth polymerization. PNIPAAm chains can be grafted with different chain lengths and densities by varying different grafting conditions. (20')



- (a) If we assume that the surface roughness remains unchanged for treated samples, compare surface **polarity and water wettability** of the treated surfaces with *pristine PP surface at room temperature* and *briefly explain*.



- (b). Propose **two** analysis methods to analyze the changes in **surface compositions** (spell out the full name)?

Pick **one** method and *sketch* out a typical figure obtained by this method (properly mark the figure, axes, and units).

Explain how the information obtained from the figure can confirm a successful grafting reaction.

- (c). Label contact angle and all interfacial tensions on the following figure. Give Young's equation and define the concept of critical surface tension?



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(d). The water contact angle of PNIPAAm-grafted PP surface will change as a function of temperature.
Predict how it will change as a function of temperature and briefly explain your answer.

(e). What is super-hydrophobicity? Discuss an approach to create such a PP surface with super-hydrophobicity.

(f). When grafting density of PNIPAAm is sufficiently high, PNIPAAm grafts form a *hydrogel layer* on the surface when water is added, generating a hydrogel surface with modulus varying with temperature. Which method can you choose to measure the modulus of this surface as a function of temperature and compare with unmodified PP? Briefly describe the method and how you could assess the surface modulus, and you may use graph to aid the description.

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7. Survey. Write your answers in the boxes. [5' bonus points]

7.1. How often do you use Piazza?

- (a). Every week; (b). Every month; (c). Rarely; (d) Never.

7.2. Do you agree that Piazza is a helpful tool to your study?

- (a). Strongly agree; (b). Moderately agree; (c) Disagree; (d). No opinion.

7.3. How often do you use the recorded lectures (for the ones that are working)?

- (a). Every week; (b). Every chapter; (c). Occasionally; (d). Rarely.

7.4. Do you agree that recorded lectures are helpful to your study?

- (a). Strongly agree; (b). Moderately agree; (c). Disagree; (d) No opinion.

7.5. Do you agree that Friday quiz questions are helpful to your study?

- (a). Strongly agree; (b). Moderately agree; (c). Disagree; (d) No opinion.

7.6. Do you agree that Team Presentations were helpful to your study?

- (a). Strongly agree; (b). Moderately agree; (c). Disagree; (d) No opinion.

7.7. Do you think we should have more extra credit opportunities?

- (a). We should have more; (b). The amount is appropriate; (c). We should have fewer; (d). We should not include team presentations.

7.8. Do you think we have sufficient recitation/review sessions?

- (a). We should have more; (b). The amount is appropriate; (c). We should have fewer; (d) No opinion.

7.9. Do you think we have sufficient problem sets this semester?

- (a). We should have more; (b). The amount is appropriate; (c). We should have fewer; (d) No opinion.

7.10. Do you think we have sufficient office hours?

- (a). We should have more; (b). The amount is appropriate; (c). We should have fewer; (d) No opinion.

8. Write two specific suggestions on how we could improve this course. [5' bonus points]**-End of exam paper-**