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Modeling stress relaxation of crosslinked polymer networks for biomaterials applications: A distance learning module

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ABSTRACT

Distance learning has become a prevalent method of delivering education to all types of student demographics. Here we present an online materials-related activity, which can be implemented into any course (traditional or online) related to chemical, mechanical, or biomedical engineering. Students use a Matlab graphical user interface (GUI) to predict the stress relaxation behavior of crosslinked biomaterials with three viscoelastic models, the Maxwell, Kelvin–Voigt, and standard linear. By analyzing provided experimental data, students evaluate the impact of crosslinking on the stress-relaxation behavior and learn the underlying molecular mechanisms that cause this behavior. Furthermore, students learn the accuracy of each model prediction by comparison to the experiment data. Overall, the activity highlights the importance of structure-property relationships in the technological advancement of biomedical materials. Our evaluation indicates that the laboratory was effectively conducted online, as it contributed to outcomes set forth for undergraduate chemical engineering students by Rowan University and ABET.

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1. Introduction

1.1. *Pedagogical background*

As more colleges and universities begin to offer distance learning formats to their students, it is important to gauge the learning effectiveness of the online format, especially in engineering, a field where students will be expected to apply theory and methodologies in a hands-on design environment. We have developed a materials-related activity that can be integrated to any online course related to chemical, mechanical, or biomedical engineering. In recent years, educational institutions have made increasing use of the internet for delivery of materials education. For instance, MIT developed a 144-credit online program in materials science and engineering (Roylance, 2004). In a reported computer-based activity, students use a Matlab graphical user interface (GUI) to characterize the mechanical behavior of a library of deformable biomaterials (Singh and Khan, 2014). In this paper, we report a module where students use a Matlab GUI to analyze the stress-relaxation behavior of crosslinked poly(vinylalcohol) hydrogels using three different viscoelastic models, the Maxwell, Kelvin–Voigt, and standard linear to study. The accuracy of each model prediction is determined by comparison to easy-to-obtain experimental data. Thus, the lab is adaptable to the face-to-face environment, as well. Students relate the results of the lab activity to a biomedical application for the hydrogels, repair of the torn meniscus. The learning objectives are to:

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- Describe the manner in which stress relaxation measurements are conducted.
- Describe the underlying molecular mechanisms of stress relaxation in polymers.
- Quantify the impact of crosslinking on the stress-relaxation behavior of a polymer network and describe the underlying molecular mechanisms that cause this behavior.
- To use a mathematical package to fit experimental data to predictive models for viscoelastic behavior.
- Describe key relationships between material science and technological advancement in the field of biomaterials.

We have implemented the activity into an entirely online course entitled *Chemical Engineering Materials*, a junior level requirement at Rowan University. We demonstrate the effectiveness of the learning activity using pre- and post-tests and student surveys.

1.2. *Meniscal tears*

The menisci are paired crescent-shaped pads of fibrocartilage in the knees. Knee meniscus injuries are quite common, often resulting from car accidents or sports injuries. Since the blood supply to the meniscus is limited, especially in its central zone, it is susceptible to permanent damage when trauma or degeneration occurs (Arnoczky and Warren, 1982; Masouros et al., 2008). Clinical treatment of meniscus injury is now trending toward replacing, rather than removing or attempting to repair, the injured tissue (Abrams et al., 2013). It is thought that complete replacement will reduce the risk of patients developing osteoarthritis (Rongen et al., 2014). The aims of using meniscus replacement are to relieve the symptoms of injury, restore biomechanical function to the knee joint, and prevent development of osteoarthritis in the long term.

1.3. *Polymers for meniscus replacement*

Numerous materials have been investigated for meniscus replacement, most of them polymers. Polymers are used because of their ability to be crosslinked, which imparts resiliency and rubber-like properties to the materials. The crosslinking also helps to prevent the polymer chains from sliding past one another during deformation, which allows for better dimensional recovery when loads are released (Rongen et al., 2014). When evaluating polymers as tissue replacements, several properties must be characterized, including biocompatibility, biodegradability, and mechanical properties. The mechanical properties most often studied are compressive, tensile, creep, stress relaxation and fatigue. It is important to have knowledge of the time-dependent behavior of polymers for the development of adequate tissue substitutes. For instance, a stress relaxation test will examine the behavior of a material over time under a constant strain.

1.4. *Hydrogels*

Hydrogels are special class of polymers. In June 2007, the Society for Biomaterials declared hydrogels “Biomaterial of the Month”. Hydrogels are three-dimensional, water-swollen structures composed of mainly hydrophilic polymers. These materials are for the most part insoluble due to the presence of crosslinks. Hydrogels are superabsorbent (they can contain over 99% water) natural or synthetic polymers. They possess also a degree of flexibility very similar to natural tissue, due to the significant water content.

1.5. *Poly(vinylalcohol) hydrogels as meniscus replacements*

A candidate material for an artificial meniscus was developed using poly(vinylalcohol) hydrogels (Kobayashi et al., 2005). Preparation of PVA hydrogels is not only simple and safe, but the methods allow for significant tailoring of mechanical properties. Aqueous solutions of PVA may be physically crosslinked by techniques that introduce hydrogen-bonded regions between adjacent polymer chains, which results in elastic hydrogels. The formation of PVA hydrogels by freeze–thaw (FT) cycles has been studied extensively. From these investigations, it has been established that the crosslink density of PVA hydrogels can be affected by the number of freeze–thaw cycles (Hassan and Peppas, 2000a,b; Merrill and Peppas, 1977). Specifically, using a higher number of freeze–thaw cycles will increase the degree of crosslinking of the hydrogel that is formed.

2. Theory

2.1. *Viscoelastic properties of polymers*

For perfectly elastic materials, the stress, σ and strain ε are related linearly through the modulus, E (Eq. (1)).

$$\sigma = E\varepsilon \tag{1}$$

Elastic behavior is represented by a spring (Fig. 1A). For an elastic solid, instantaneously increasing the stress to a constant value will cause the solid to deform to a fixed strain, which does not vary with time. If the stress is removed, the material instantly recovers its original shape.

On the other hand, Newton’s Law describes the behavior of viscous materials, like silly putty. The stress is linearly related to the strain rate $d\varepsilon/dt$ through the viscosity, η, (Eq. (2)). According to this equation, the stress needed to deform a material depends on how fast the load is being applied. Higher rates of deformation require higher stresses. In addition, at a constant stress, the strain rate becomes constant. Once unloaded,

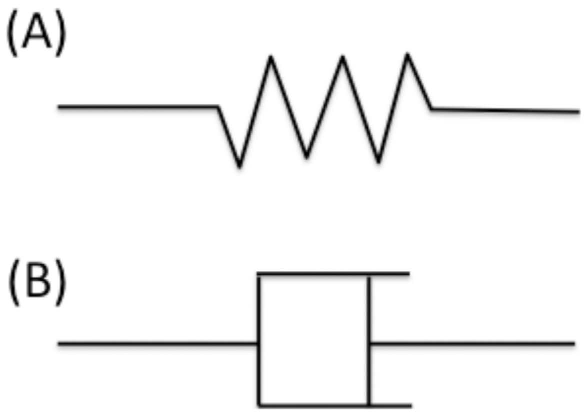

Fig. 1 – Elements of rheological models. (A) A spring, representing elastic behavior and (B) a dashpot, representing viscous behavior.