Cold flow in PLA and PETG

Tiffany Huff*
University of Texas at Austin, Department of Physics

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This work seeks to explain the general behavior of plastic materials, specifically regarding stress and creep, a solid material's tendency to permanently deform when subjected to persistent stress. Creep obeys Hooke's law, and stress and strain are directly proportional. If the mechanical stress on the material is known, then creep is well understood and predicted by assuming a simplified model of the material's molecules, representing their motion using normal modes.

In addition, comparing this behavior in the materials Polylactic Acid (PLA) and Polyethylene Terephthalate Glycol (PETG) in our experimental setting to investigate suitability, we found that due to its higher temperature resistance and stress tolerance, PETG was preferable. We also examine their behavior over time and predict how these materials will respond under experimental conditions.

I. PLASTICS

A. Introduction

The term plastic includes many partially or entirely synthetic materials, typically consisting of mainly polymers, produced by industrial means from fossil fuel based petrochemicals. [1] During this production, plasticity, the ability for a material to permanently change shape in response to an external force, allows for the material to be manipulated. [1]

The materials science of plastics has been explored by many chemists, notably Hermann Staudinger, "the father of polymer chemistry", and Herman Mark, "the father of polymer physics". Leo Baekeland created the term "plastics" and produced the first fully synthetic plastic in 1907. [2]

Modern uses for plastics include packaging, construction, automobiles, furniture, electronics, and 3D printing. In addition, the medical field uses plastic for polymer implants and other devices. Typical types of plastics include polyethylene, used in packaging, and polyvinyl chloride, used in piping and construction. [2]

B. Polymers

A polymer's structure is described by its constituent monomers, or smallest individual units, as well as its microstructure, or the configuration of these monomers in a single chain within the polymer. [1] The chemical and physical properties of a polymer are mostly determined by the polymer's ability to form state phases with various configurations, which is dependent on the microstructure. [1]

The elasticity of the polymer is quantified by Young's modulus, the rate of change in stress to strain. [3] Hooke's law of linear elasticity is given by

$$\sigma = E\epsilon, \tag{1}$$

where σ is stress, E is Young's modulus, and ϵ is strain. [4]

C. Polymer Chain Modelling

Polymer chains are represented by "ideal" or "real" models. Ideal chains assume no chain monomer interactions, valid for polymeric systems where positive and negative monomer interactions cancel. [1]

Real chains refer to modelling chain monomer interactions as excluded volume, the idea that one part of a long chain molecule cannot occupy space that another part of the same molecule is already occupying, leading to a reduction in the possible configuration and a self-avoiding random walk. [1]

The average distance from the chain to the center of the chain's mass, the radius of gyration, is used to express the space the polymer molecule occupies. This can also be represented in terms of the pervaded volume, the volume spanned by the chain, which scales with the cube of the radius of gyration. [1]

Reptation is the process by which individual macromolecules move through a polymer matrix. The movement of a chain molecule in a virtual tube is constrained by entanglements with neighboring chains. [**?**]

D. Creep

Stress relaxation refers to how a material relieves stress when undergoing constant strain. Stress σ is given by

$$\sigma = \frac{F_n}{A}, \tag{2}$$

and strain ϵ is given by

* tiffany.huff@utexas.edu

$$\epsilon = \frac{\delta L}{L_0} = \frac{L - L_0}{L_0}, \tag{3}$$

where F_n is the applied force and A is the cross-sectional area, δL is the change in length, L_0 is the original length, and L is the final length. [4]

In materials science, creep or cold flow refers to the behavior of solid materials when under persistent stress. [5] In some applications, creep can be desirable, such as to prevent snapping or cracking. [2] This tendency is intensified when the material is exposed to heat for substantial periods of time, increasing near the material's melting point. [5]

Each material has a specific range of temperatures for which creep deformation occurs. Materials generally exhibit creep deformation at temperatures near their melting point or when stressed. [5]

Creep occurs in three stages. First, the strain rate is a function of time during primary creep. Then in secondary or steady-state creep, the strain rate is constant. Finally, the strain rate increases exponentially with stress in tertiary creep. [5]

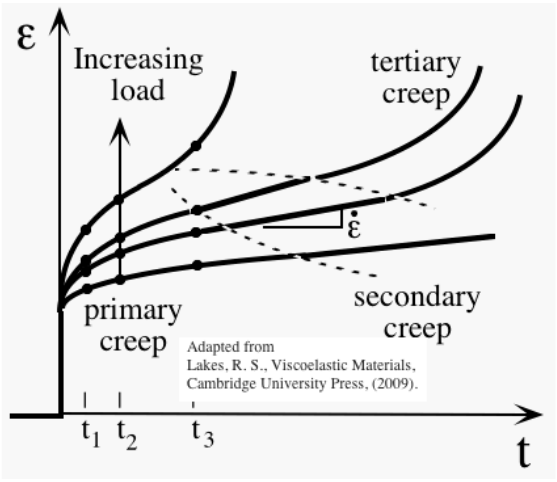

FIG. 1. The three stages of strain as a function of time as a result of constant long-term stress [6]

There are various mechanisms of deformation that could occur depending on temperature and nature of stress. [5] Generally,

$$\frac{d\epsilon}{dt} = \frac{C\sigma^m}{d^b} e^{\frac{-Q}{kT}}, \tag{4}$$

where ϵ is creep strain, C is a constant dependent on creep mechanism and material, m and b depend on mechanism, Q is creep mechanism activation energy, σ is applied stress, d is the material's grain size, and T is absolute temperature. [5]

1. Creep in Polymers

When a polymetric material undergoes an abrupt force, the Kelvin-Voigt model depicts the response by representing the material as a Hookean spring in parallel with a purely viscous damper, shown in figure 2. [5]

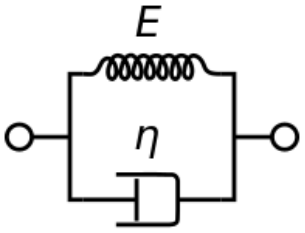

FIG. 2. Diagram of Kelvin-Voigt model [7]

The strain on each component in this model is equivalent and given by

$$\epsilon_{Total} = \epsilon_S = \epsilon_D, \tag{5}$$

where ϵ_S represents the stress-strain in the spring and ϵ_D in the damper. The stress is given by

$$\sigma_{Total} = \sigma_S + \sigma_D, \tag{6}$$

These are related by equations with form

$$\sigma(t) = E\epsilon(t) + \eta\frac{d\epsilon(t)}{dt}, \tag{7}$$

where E is the elasticity modulus and η is viscosity. [4]

If an instantaneous, constant stress σ_0 is applied to this Kelvin-Voigt object, the material's deformation will approach the deformation of the pure elastic material with an exponentially decaying difference:

$$\epsilon(t) = \frac{\sigma_0}{E}(1 - e^{-\lambda t}), \tag{8}$$

where t is time, and λ is the rate of relaxation $\lambda = \frac{E}{\eta}$. [4]

The creep strain relationship is given by

$$\epsilon(t) = \sigma C_0 + \sigma C \int_0^\infty f(\tau)(1 - e^{-\frac{t}{\tau}})d\tau \tag{9}$$

where σ is applied stress, C_0 is the instantaneous creep compliance, C is the creep compliance coefficient, τ is the retardation time, and $f(\tau)$ is the distribution of retardation times. [5]

A viscoelastic material under constant, maintained stress for sufficient period of time at t_0 will increase strain in response to stress until the material fails. [5]

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