

Cold flow in PLA and PETG

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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.

Additionally, when comparing this behavior in the materials Poly(lactic Acid) (PLA) and Poly(ethylene 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 examined and predicted how these materials would behave over time to determine if they would withstand our experimental conditions for at least ten years and again found that PETG was the better choice.

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. [3] 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. [4] Hooke's law of linear elasticity is given by

$$\sigma = E\epsilon, \quad (1)$$

where σ is stress, E is Young's modulus, and ϵ is strain. [5]

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. [6]

D. Creep

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

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$$\sigma = \frac{F_n}{A}, \quad (2)$$

and strain ϵ is given by

$$\epsilon = \frac{\delta L}{L_0} = \frac{L - L_0}{L_0}, \quad (3)$$

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. [5]

In materials science, creep or cold flow refers to the behavior of solid materials when under persistent stress. [7] 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. [7]

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. [7]

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. [7]

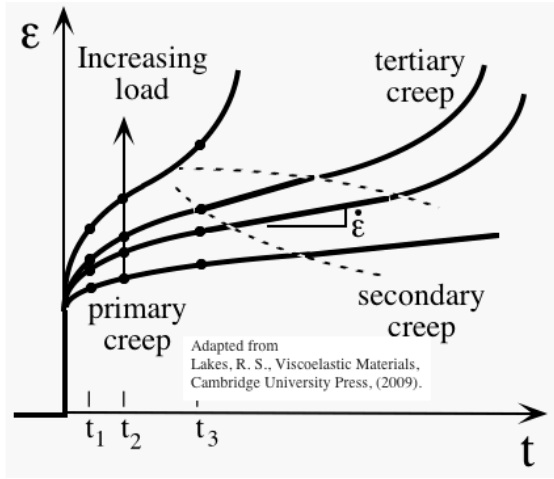


FIG. 1. The three stages of strain as a function of time as a result of constant long-term stress [8]

There are various mechanisms of deformation that could occur depending on temperature and nature of stress. [7] Generally,

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

where ϵ is creep strain, C is a constant dependent on creep mechanism and material, m and b depend on mech-

anism, Q is creep mechanism activation energy, σ is applied stress, d is the material's grain size, and T is absolute temperature. [7] The activation energy Q can be determined experimentally by plotting the natural log of creep rate against the reciprocal of temperature. [9]

1. Creep Mechanisms

The process by which creep occurs in a material can vary. Creep mechanisms for steady state creep are diffusion and dislocation creep. [9] Since all steady-state creep mechanisms are dependent on diffusion which is governed by the Arrhenius equation,

$$D = D_0 e^{-\frac{Q}{RT}}, \quad (5)$$

where R is the gas constant, then the creep rate must have an exponential dependence on temperature as shown in equation 6. [9]

$$\dot{\epsilon} \propto e^{-\frac{Q}{RT}} \quad (6)$$

The stress dependence of the rate of creep deformation generally increases with

$$\dot{\epsilon} \propto \sigma^n, \quad (7)$$

where n is called the stress exponent and depends on creep mechanism.

Total creep is given by

$$\epsilon_T = \epsilon_E + \epsilon_C, \quad (8)$$

where ϵ_E is the elastic strain and ϵ_C is the inelastic strain. [9] Then,

$$\dot{\epsilon}_C = mBt^{m-1}\sigma^n, \quad (9)$$

where B , m , and n are empirically determined constants. [9] In the time independent form

$$\dot{\epsilon}_C = \frac{mB^{1/m}\sigma^{n/m}}{\epsilon_c^{(1-m)/m}}. \quad (10)$$

2. 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. [7]

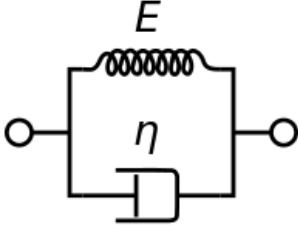


FIG. 2. Diagram of Kelvin-Voigt model [10]

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

$$\epsilon_{Total} = \epsilon_S = \epsilon_D, \quad (11)$$

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

$$\sigma_{Total} = \sigma_S + \sigma_D, \quad (12)$$

These are related by equations with form

$$\sigma(t) = E\epsilon(t) + \eta \frac{d\epsilon(t)}{dt}, \quad (13)$$

where E is the elasticity modulus and η is viscosity. [5]

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:

$$\epsilon(t) = \frac{\sigma_0}{E} (1 - e^{-\lambda t}), \quad (14)$$

where t is time, and λ is the rate of relaxation $\lambda = \frac{E}{\eta}$. [5]

The creep strain relationship is given by

$$\epsilon(t) = \sigma C_0 + \sigma C \int_0^\infty f(\tau) (1 - e^{-\frac{t}{\tau}}) d\tau \quad (15)$$

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. [7]

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. [7] For shorter periods of time, the material will strain initially until a time t_1 when the stress is removed, then the strain immediately discontinuously decreases, shown in figure 3. [7]

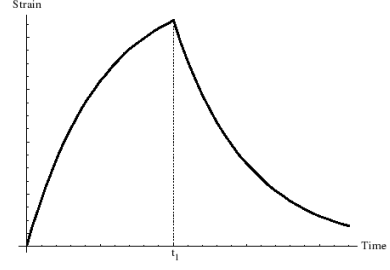


FIG. 3. Dimensionless deformation's dependence on dimensionless time under constant stress [10]

Additionally, a polymer's molecular weight impacts the creep behavior. Higher molecular weight leads to an increase in creep resistance in polymers due to the higher amount of secondary bonding between polymer chains. [5]

II. CREEP IN PLA AND PETG

PETG is made from a glycol-modified variant of PET, Polyethylene Terephthalate, through copolymerization offering greater printability and toughness. [3]

The type of creep exhibited by PET (and PETG) is determined by the type of polymer comprising the molecule. Polyesters and aramids exhibit time-logarithmic creep, as opposed to ultra high molecular weight polyethylene which exhibits time-linear creep. [6]

When tested over a large range of temperatures and strain rates, PET and PETG were found to have similar responses. Below the glass transition temperature, the materials exhibited stress-strain behavior of a distinct yield stress, then strain softening followed by moderate strain hardening at moderate levels of strain, and dramatic strain hardening at large strains. [11] The primary hardening and stiffening mechanism in both PET and PETG is molecular orientation. [11]

PETG has more desirable thermal and mechanical properties than regular PLA and thus is more commonly used for longer term experiments. [12] In comparison to PLA, PETG has the lower rate of decay and thus is preferable when long term elasticity is required. [7] In addition, PETG withstands higher temperatures than PLA. [12] When tested on the effects of build orientation, layer thickness, and feed rate, PETG showed a stronger stress-strain response than PLA. [13]

A. Thermomechanical Behaviors of PETG

The stress-strain curves for PETG under strain rates of 0.003/s and 0.0001/s at 20°C is shown in figure 4.

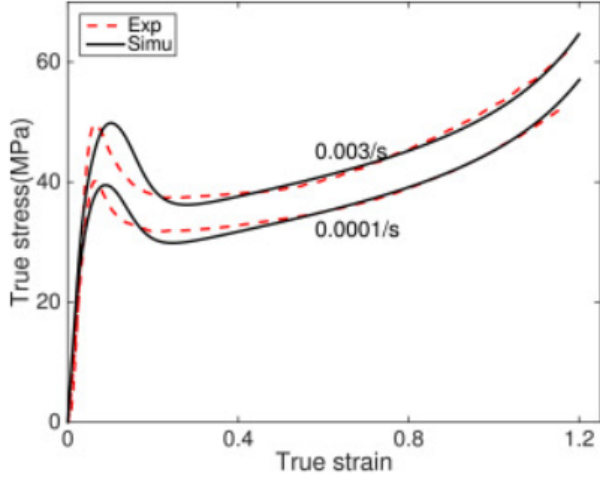


FIG. 4. Stress-strain curves for PETG under strain rates of at 20 degrees celsius [13]

There is little published regarding the mechanical behavior of PETG and no models proposed to represent the deformation behavior. However, the experimental data that has been collected over the effects of various stress tests on different properties of PETG found that the geometry of these defects could also affect the strain localization and failure of PETG, as shown in figure 5. [3]

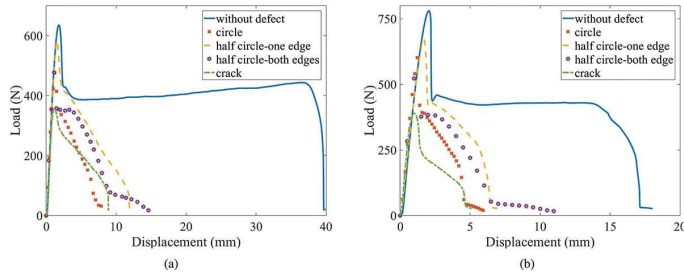


FIG. 5. Stress response of PETG with various geometric defects [13]

Additionally, predeformation temperature significantly affects the material's strain hardening response. [13] The stress strain-curves of PETG for various temperatures and strains is shown in figure 6.

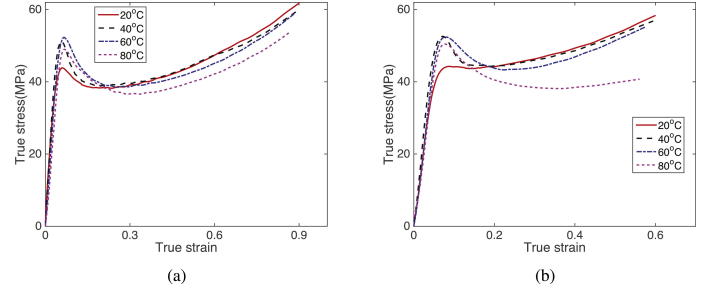


FIG. 6. Stress-strain curves for PETG at different temperatures for a strain of (a) 30% and (b) 60% [13]

Table one lists the values for multiple properties of PETG and PLA. Toughness is calculated by integrating the stress-strain curve of the material. [14]

TABLE I. Thermal and Tensile Properties of PETG and PLA

| Property | PETG | PLA |
|---------------------------|--------------|--------------|
| Tensile Modulus | 2.1GPa | 2.3GPa |
| Tensile Strength | 45.8MPa | 26.4MPa |
| Tensile Strength at Yield | 53MPa | 35.9MPa |
| Elongation at Yield | 14% | 2% |
| Elongation at Break | 18% | 4% |
| Flexural Strength | 70 MPa | 61.8 MPa |
| Young's Modulus | 2.2 GPa | 3.5 GPa |
| Glass Transition T_g | 82°C | 57°C |
| Heat Capacity | 1200J/kg · K | 8200J/kg · K |
| Thermal Conductivity | 0.29W/m · K | 0.13W/m · K |

Other considerations regarding PETG is that it is hygroscopic, or absorbs moisture from the air. [13] The mechanical performance of PLA is also adversely affected by moisture absorption. [13]

III. CONCLUSION

Creep, or cold flow, is the property of solids referring to a material's response to long-term force and is dependent on temperature, material, and the nature of the stress. We found that the creep behavior of PET is comparable to PETG, an amorphous copolymer of PET. [11]

We also determined that PETG would likely be the more desirable material over PLA due to its higher temperature and stress response by comparing various thermal and tensile properties of the materials. When investigating other common materials used for 3D printing, we found that when compared PETG had the best properties for our experimental purposes.

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