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An Overview of Mechanical Properties and Material Modeling of Polylactide (PLA) for Medical Applications

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Abstract

This article provides an overview of the connection between the microstructural state and the mechanical response of various bioresorbable polylactide (PLA) devices for medical applications. PLLA is currently the most commonly used material for bioresorbable stents and sutures, and its use is increasing in many other medical applications. The nonlinear mechanical response of PLLA, due in part to its low glass transition temperature ($T_g \approx 60°C$), is highly sensitive to the molecular weight and molecular orientation field, the degree of crystallinity, and the physical aging time. These microstructural parameters can be tailored for specific applications using different resin formulations and processing conditions. The stress-strain, deformation, and degradation response of a bioresorbable medical device is also strongly dependent on the time history of applied loads and boundary conditions. All of these factors can be incorporated into a suitable constitutive model that captures the multiple physics that are involved in the device response. Currently developed constitutive models already provide powerful computations simulation tools, and more progress in this area is expected to occur in the coming years.

INTRODUCTION

Bioresorbable polymers, such as polylactide (PLA) and polyglycolide (PGA), play an increasingly important role in biomedical applications due to their unique ability to be completely resorbed *in-vivo* in a material-specific time frame ranging from months to a few years. Furthermore, the ability to tailor their mechanical, microstructural, chemical, and degradation properties for specific applications has catalyzed an extensive and growing amount of research aimed at utilizing these materials in innovative ways and applications [1]. Of all biodegradable polymers, PLA is the most widely produced [1]. Polylactide (PLA) is an aliphatic polymer that exists as two stereoisomers: poly (L-lactide) acid (PLLA) and poly (D-lactide) acid (PDLA), or as a racemic mixture, designated as PDLLA [2]. Table 1 summarizes some of the most commonly used bioresorbable polymers. The properties of PLA can be modified by many different methods, including: variations in the L/D ratio of isomers, co-polymerization with other monomers (such as glycolide and caprolactone), adding plasticizers, adding fillers, and thermal heat treatments [3] [4]. PLA is used in a wide range of biomedical applications such as stents [5] [6] [7] [8], sutures [9], screws [10], nails, pins, anchors [11], spinal cages [12], soft-tissue implants, tissue engineering scaffolds, drug delivery devices [13], and craniofacial augmentations in plastic surgery [14]. In all of these applications the PLA is exposed to different device-specific load environments.

A bioresorbable stent, for example, is exposed to very large stresses and strains during the crimp and expansion steps. After deployment the stent typically contains large viscoplastic residual strains. Additionally, it needs to maintain its mechanical integrity when exposed to a large number of load cycles with low stress and strain amplitudes. The most commonly used material for bioresorbable scaffolds (BRS) is poly-L-lactic acid (PLLA) [15]

[16] [7]. The first use of PLLA in this application *in vivo* was the Igaki-Tamai stent [8]. Other current generation PLLA stents include the ABSORB Bioresorbable Vascular Scaffold (Abbott Vascular, Santa Clara, CA), the DESolve bioresorbable scaffold (Elixir Medical Corporation, Sunnyvale, CA), and Amaranth (Amaranth Medical Inc., Mountain View, CA). However, there are many challenges that are encountered during the use of bioreseorbable stents. Although stent technology is well established and the mechanical behavior of metallic stents has been well characterized, the use of degradable, non-linear, viscoplastic materials presents many new challenges to the development and use of bioresorbable stents by altering the mechanical response of the devices to their *in vivo* environments. Due to the lower stiffness and strength of PLLA compared to metals, the struts are typically required to be thicker than what is used with conventional metal stents in order to obtain the desired radial strength. This may lead to poor deliverability, platelet deposition, and vessel injury. Despite these difficulties, BRS have many advantages when compared to their traditional counterparts. The main advantage of these devices is that no foreign body remains in the vessel indefinitely, hence eliminating the risk for very late stent thrombosis. Other benefits include improved noninvasive imaging (tomography and magnetic resonance imaging), and less restrictions on future interventions since there is no interference with previously implanted drug eluting stents [6].

The challenges associated with PLA used in orthopedic applications are different and highly dependent on the location and type of device in use. In most cases orthopedic devices are designed to withstand large and repeated compressive stresses. Typical devices are composed of steel or titanium to ensure that the devices are capable of withstanding in vivo loading over long periods of time [17]. However, the high mismatch between bone and implant strength leads to stress shielding and the bone degeneration associated with loosening of implants over time.

Biodegradable implants are an attractive alternative which would provide a temporary support while allowing long-term tissue growth. This alternative is particularly attractive when orthopedic devices are implanted in children where patient growth can lead to the need for removal or a replacement implant [18]. PLLA is a common choice for many of these applications due to its long degradation time and nontoxic nature. Studies comparing the strength of these degradable devices to their metallic counterparts have found similar success rates [18] [19] [20]. In these applications it is important that the applied stress never gets so large that the implant undergoes significant permanent deformation, or premature failure due to viscoplastic flow or fracture.

Another common application of PLA is in bioresorbable sutures. In this application a surgeon imposes a small radius of curvature but due to the even smaller suture diameter the strains are often small. Similarly small stresses and strains are typical of soft tissue applications.

It has recently been shown that the rate of degradation of PLA is dependent on the magnitude of the applied stress [21] [22]. An additional complication is that PLA can exhibit premature failure at stress magnitudes that are significantly lower than both the yield strength and the ultimate tensile strength of the material due to viscoplastic flow causing creep rupture or fatigue failure. As a result, in some applications device failure can occur long before the material is expected to fail due to degradation *in vivo*. In order to address these challenges it is necessary to fully understand the mechanical response of these new generation medical devices that incorporate bioresorbable components. This requires in-depth characterization of how the strength and stiffness of the material change due to time-dependent microstructural mechanisms, how the material response changes during degradation, and how the material undergoes non-

linear viscoplastic deformations at finite deformations. These insights are required in order to guide and validate medical device designs, and are the topics of the following sections.

MECHANICAL PROPERTIES OF POLY(LACTIC ACID)

The mechanical response of PLA and other bioresorbable polymers is highly non-linear due to a strong dependence on temperature, molecular weight, molecular orientation, crystallinity, and physical aging characteristics. It is critically important to understand these behaviors and how they influence the material response in order to properly design a medical device, and to analyze the device response under realistic *in-vivo* conditions. There have been many studies aimed at elucidating the polymerization techniques [1], thermal transitions and crystallization behaviors [23], stereochemistry [2], and rheological properties of PLA and PLA blends [24]. Less research has been aimed at extracting the mechanical properties of relevance for biomedical applications. There is a large overlap and synergy between the chemistry, material science and mechanical properties of PLA, which will be summarized in this section.

Temperature Dependence and Physical Aging

One of the main drivers of the non-linear response of PLA is the proximity between normal usage temperatures (room temperature and body temperature) and the glass transition temperature, which is typically between 55°C and 65°C. At body temperature the thermal energy is sufficiently large that the material response may either be stiff and brittle, or ductile and viscoplastic depending on the processing conditions, molecular structure, and thermal heat treatments. As an example, Figure 1 shows the results from dynamic mechanical analysis (DMA) temperature sweeps [25] illustrating that the small strain storage modulus is very slowly

decreasing with increasing temperature until reaching the glass transition temperature at which the modulus decreases by more than two orders of magnitude in a narrow temperature range. The exception to this behavior is highly drawn PLLA monofilaments which due to their high degree of crystallinity undergo a much less severe reduction in stiffness [25]. The increase in storage modulus that is observed in some PLLA above the glass transition temperature is due to cold crystallization caused by the increased molecular mobility at these elevated temperatures [26] [27] [28]. Evidence of cold crystallization can also be seen in some differential scanning calorimetry (DSC) measurements [28]. Rapidly cooling PLLA through its glass transition temperature after part manufacture significantly slows the molecular mobility, essentially freezing the structure of the amorphous domains and effectively reducing molecular alignment in the material. The microstructure will then, over time, undergo slow rearrangements in order to reduce its enthalpy. This gradual molecular rearrangement is called physical aging and occurs in all glassy polymers [29]. The magnitude of physical aging can be assessed through DSC scans. Figure 2 shows DSC data for PLLA which has been aged for different times [26] [27]. The glass transition exhibits a monotonic enthalpic transition in the unaged sample. Physical aging in the material is manifested as the presence of an endothermic overshoot at T_g and a shift in the endothermic peak to higher temperatures with increasing aging time. The physical mechanism driving these behaviors is the volume relaxation accompanied by a reduction in free volume and enthalpy. During subsequent heating more energy is required to go through the glass transition causing the increased endothermic peak. Furthermore, the reduction in segmental mobility shifts the glass transition temperature to slightly higher temperatures. The aging state of the material also has a strong effect on the mechanical properties of PLLA. A study by Pan et al. [26] demonstrated that unaged PLLA has an elongation to failure of 300% at room temperature. After

aging at room temperature for 144 hours the elongation to failure was reduced to 4.4%. During physical aging the yield stress and the tensile modulus also increase [26]. Note that physical aging does not cause a change in crystallinity. These results suggest that it might be possible to increase the ductility of PLLA by reducing the physical aging using branched PLLA molecules, or crosslinking the material effectively decreasing the molecular mobility. However, as has been shown by Maharana et al. [30], radiation induced cross-linking in the presence of multi-functional coagents can lead to property reductions independent of ageing. Using chain branching to slow aging processes appears more promising. Nerker at al. [4] demonstrated that long chain branching by a radical mediated grafting in the melt state can create enhanced strain hardening and crystallinity. The aging process is of particular interest since changes in the mechanical properties of a biodegradable device during storage can affect how the device performs *in vivo*. Understanding the aging process and predicting the changes in mechanical properties are important for determining the shelf life of an unused device.

Molecular Orientation and Crystallinity

Like all glassy polymers, both the stiffness and ductility of PLA is highly dependent on the molecular orientation and degree of crystallinity of the microstructure. Figure 3 shows the correlation between Young's modulus and elongation to failure at room temperature for PLA materials with different microstructural states. PLLA fibers have a highly oriented microstructure and a high degree of crystallinity. Due to these characteristics the Young's modulus is typically between 3 and 7 GPa, and the elongation to failure varies between 20% and 100%. Fibers with higher modulus typically have a lower ductility. At room temperature pure PLLA typically exhibit a stiffness between 3 and 4 GPa, and an elongation to failure that is less

than 10%. As was shown by Pan [26], unaged amorphous PLLA can have an elongation to failure exceeding 150%, yet still have a Young's modulus of 3 GPa. Many industrially used PLLA components have a Young's modulus between 500 and 2 GPa, and an elongation to failure from 20% to 150% [31] [32] [33]. However, these resins are often co-polymers with other bioresorbable polymers such as poly(ε-caprolactone) (PCL), or include plasticizers like poly(ethyline-glycol) (PEG) to increase the ductility.

Molding and extruding parts from a bioresorbable polymer can lead to a molecular orientation field that is aligned in the flow direction. This orientation field can have a strong influence on the mechanical properties, including stiffness and ductility. Process parameters, such as stretch ratio and tube expansion, can be used to tailor the mechanical response of a medical device in its manufactured state. Figure 4 shows one example of the anisotropic effects that can be observed due to a molecular orientation field [32]. In this case tension specimens were die cut from a 1 mm thick sheet of PLLA in two orthogonal directions (0° and 90°). The specimens were then pulled at room temperature to 2.5% strain, unloaded to zero stress, reloaded to 4.5% strain, unloaded to zero stress, and then monotonically loaded to failure. The applied strain rate in these tests was 0.01/s. The stress-strain data show that the material is non-linear viscoplastic, and that the material response is anisotropic with different Young's moduli and yield stress values in the two orthogonal directions. As expected, the stiffness and yield stress is also significantly reduced at a temperature of 40°C compared to room temperature.

Time-Dependent Effects

All thermoplastic materials, including PLLA and poly(L-co-glycolide) (PLGA)

[34] creep at applied strains that are lower than the yield strain. This relaxation process can have a significant effect on device behavior but is not accounted for by purely elastic models of material behavior. Although the experimentally observed stress-strain behavior in thermoplastic materials is characterized by an initial linear elastic or linear viscoelastic response, nonlinear and viscoplastic behavior develop over time. Since the material is in a glassy state, there will always be a stochastic distribution of free volume, energy barriers, and shear transformation sites. The sites with the lowest energy barriers have a greater probability for local shear transformation events (local yielding). As the stress increases transformations start to occur at meaningful rates causing a non-linear stress-strain response. During these events the surrounding material will exert a back stress on the transformed regions, causing a further increase in the activation barrier for viscoplastic flow. When the material is unloaded these back stresses cause a highly non-linear unloading response and recovery (shown in Figure 4). If instead of being unloaded, the material is loaded further (Figure 5) there may come a point where the distributed yielding has spread through a large portion of the material causing a reduction in the activation energy spectrum for these transformation sites. This leads to stress softening and localized deformation (necking) if the loading mode is uniaxial tension. At very large strains, before failure, the stress may increase as deformation induced orientation in the microstructure reduce entropy in the material. These behaviors are clearly shown in the data from Smit [35] plotted in Figure 5. This figure is particularly interesting in that is shows a very significant drop in the stress magnitude after macroscopic yielding in uniaxial compression. This behavior is unusual for thermoplastics and does not imply that the material response becomes geometrically localized during the loading. Instead the stress softening is a manifestation of the strong drop in the activation energy spectrum after yielding.

These behaviors have a multitude of significant consequences for the material behavior. For example, as was shown by Smit [35], if the same PLLA that was examined in Figure 5 is compressed to a true stress of -50 MPa, which is below the macroscopic yield stress, then the material will slowly start to creep. Figure 6 shows that after being subjected to that load for approximately 35 min the strain magnitude suddenly starts to increase rapidly. This behavior can be understood based on the energy activation argument presented above. Even if the load is below the macroscopic yield stress there is a certain probability for localized yielding that over time through stochastic processes will lead to the accumulation of viscoplastic creep strain. Once a critical amount of shear transformations have taken place the overall activation energy spectrum will drop causing the experimentally observed rapid increase in strain which leads to macroscopic failure. The implications for devices, such as bioresorbable scaffolds or bone screws, which experience a constant load *in vivo* are significant.

The energy activated yielding processes also indicate that the yield stress is strain-rate dependent. This is examined in detail by Söntjens et al. [36] who demonstrated that both the time to failure under constant stress and the strain-rate dependent yield stress can be accurately predicted using the Eyring energy activation model [37] modified to include the number average molecular weight (M_n):

$$\dot{\varepsilon}_p = \dot{\varepsilon}_0 \exp\left(-\frac{\Delta U}{R\tilde{T}}\right) \sinh\left(\frac{\sigma V}{k_B \tilde{T}}\right), \quad (1)$$

where $\dot{\varepsilon}_p$ is the viscoplastic flow rate, $\dot{\varepsilon}_0$ a reference strain rate that is introduced for dimensional reasons, ΔU is the activation energy, R the universal gas constant, T is the temperature, K_g the Fox-Flory constant, M_n the number average molecular weight, $\tilde{T} = T + K_g/M_n$ is an effective temperature that depends on the molecular weight, σ the applied stress, V

the activation volume, and k_B is Boltzmann's constant. Söntjens et al. [36] demonstrated that if this flow equation is calibrated properly then it can be used to predict the influence of molecular weight on the stress-strain response and the creep rupture time.

Similar experimental results were obtained by Dreher at al. [34] who studied the load dependent creep behavior of PLLA and PLGA under physiologically relevant loading rates. An important conclusion of these observations is that bioresorbable medical devices exposed to long-term loading *in vivo* can experience failure at an earlier stage than what would be predicted using traditional simple non-linear elastic or plastic analysis which do not account for these accumulating yield processes.

Degradation Behavior

The degradation behavior of PLA is a critical characteristic of the material and the most important reason for the high interest in its use in medical applications. PLA belongs to the group of polyesters, and has a relatively long half-life of hydrolysis due to steric effects where the alkyl group hinders the attack by water [38]. For example, PLLA stent fibers exposed to *in-vivo* conditions do not begin to degrade until after approximately 12 month [39] [40].

The main degradation mechanism of PLA is hydrolysis. It can be an autocatalytic process when the degradation product, carboxylic acid, is trapped causing localized increases in pH and where the lactic acid helps to catalyze the hydrolysis process [41]. The stereochemistry, crystallinity, molecular weight, and applied loads are the main factors influencing the rate of degradation of PLA [42] [43]. The degree of crystallinity is greatly important for the degradation rate since the crystalline domains are less permeable to water and hence undergo slower hydrolysis [44]. It has recently been shown that the rate of degradation is also dependent on the

magnitude of the applied stress [21] [22]. During degradation the yield strain, yield stress, and elongation to failure all decrease [21]. These changes in yield stress, yield strain and elongation at failure can have consequences for devices which are load bearing throughout their degradation process. Although the artery is thought to remodel after approximately 6 months, device fractures or viscoplastic flow may cause uneven loading in the vessel which could have a negative impact on a tissue which is highly sensitive to changes in the mechanical environment.

MATERIAL MODELS

The highly non-linear mechanical response of PLA and other bioresorbable polymers obviously has a strong influence on the performance of any medical devices where this class of materials is used. Despite this importance there has only been a limited amount of research devoted to developing material models capable of capturing the experimentally observed material behavior under physiologically relevant conditions. The material model frameworks examined in this section are compared in Table 2.

One of the pioneering efforts in the area was developed by Soares, Moore, and Rajogopal [39] [45]. The focus of their work was on developing a deformation induced degradation model. Here, degradation is caused by scission of chemical bonds in the macromolecules resulting in a reduction in molecular weight and the Young's modulus. The starting point of their model is an incompressible, isotropic neo-Hookean hyperelastic material model representing the base state of the material. The material stiffness is made dependent on a scalar degradation parameter, d, representing the fraction of broken bonds at a given location: $\mu = \mu_0 (1-d)$, where μ_0 is the shear modulus of the non-degraded material. The evolution in degradation is strain dependent and is represented using the following equation:

$$\frac{d}{dt}(d) = C[1-d]\sqrt{(I_1-3)^2+(I_2-3)^2} \quad (2)$$

where C is material parameter, I_1 the first invariant of the left Cauchy-Green tensor [46], and I_2 the second invariant of the left Cauchy-Green tensor. As discussed by Soares [45], this phenomenological representation of the damage evolution is among the simplest possible while still being adequate for their study.

A more recently developed model framework from the same group [46] [21] used the Knowles hyperelastic material model [47] [48] where the Helmholtz free energy per unit reference volume (ψ) is given by:

$$\psi(I_1) = \frac{\mu}{2b}\left[\left(1+\frac{b}{m}(I_1-3)\right)^m - 1\right] \quad (3)$$

where μ is the shear modulus, and b and m are material parameters. The Knowles hyperelastic model is a phenomenological representation that is convenient in that is allows for highly non-linear stress-strain predictions. The material parameters are taken to evolve with the damage state (d) following: $\mu(d) = \mu_0 (1-d)$, $b(d) = b_0 (1-d)$, $m(d) = m_0 (1-d)$. These simple equations were selected by Soares et al. due to the unavailability of more detailed experimental data. Their proposed model framework is promising in that it allows for direct predictions of the stress response due to the evolution in damage. The main limitation of their work is that it is based on a non-linear elastic representation of the basic material response giving a stress response that is virtually independent of applied strain rate, and an unloading response that is virtually identical to the loading response. Experimentally, PLA and other bioresorbable polymers have been shown to exhibit a non-linear viscoplastic response in both its virgin and degraded state.

A different constitutive model framework was developed by Khan and El-Sayed [49]. Their goal was to create a phenomenological nonlinear viscoelastic model for generic

biodegradable polymers under regimes with large deformations. The proposed model consists of a compressible Ogden hyperelastic network in parallel with a number of Maxwell elements all with Ogden hyperelastic components. The rate equation of material degradation is taken from Equation (2) above that was originally proposed by Soares. The shear modulus, and other material parameters are then assumed to evolve with the degradation state, for example: $\mu = \mu_0$ (1-*d*). This constitutive model is interesting in that it includes both non-linear elasticity, degradation, and linear viscoelasticity. The main limitation of the model framework is that the viscoelastic response is based on simple linear viscoelasticity, when it is known that the large strain response of glassy thermoplastics is never linear viscoelastic [48].

An physically motivated material model for PLA was developed by Söntjens et al. [36]. This material model uses a modified Eyring energy activation approach, see Equation (1), to represent the rate of viscoplastic flow as a function of the applied stress, temperature, and molecular weight. A thermomechanical constitutive model based on this flow equation can be formulated using results outlined by Sturm et al. [12] and Klompen et al. [50] [51]. This material model framework can be implemented as a user-material model for finite element simulations. One of the more interesting features of this model is that it incorporates degradation effects through molecular weight reductions in a more physically motivated way than the Soares et al. models [45] [39].

An advanced anisotropic non-linear viscoplastic constitutive model for PLLA was developed by Eswaran et al. [52]. This material model was specifically developed for computational modeling of bioresorbable stents, where the aim of the modeling was to help with design iterations and optimization, and also reduce the need for bench-top testing. The proposed material model framework can be represented using two parallel rheological networks, where

one network (A) is anisotropic hyperelastic, and the second network (B) consists of a simple hyperelastic model is series with a micromechanism inspired flow component. This two-network rheological structure is the same as the approach used by Söntjens et al. [36], but the details of the Eswaran model components are different. The kinematics of this model framework is also the same as the Bergstrom-Boyce model [53], but the components of the model have been changed to fit the response of PLA materials.

In the Eswaran model the stress in Network A is given by the neo-Hookean hyperelastic model:

$$\boldsymbol{\sigma}_A = \frac{\mu_A}{J_A^e}\,\mathrm{dev}[\boldsymbol{b}_{\boldsymbol{A}}^{\boldsymbol{e}*}] + \kappa(J_A^e - 1)\mathbf{I}, \tag{4}$$

where $[\mu_A, \kappa]$ are material parameters, $J_A^e = \det[\boldsymbol{F}_A^e]$, $\boldsymbol{b}_{\boldsymbol{A}}^{\boldsymbol{e}*}$ is the distortional left Cauchy-Green tensor of the elastic part of the deformation gradient. The stress in Network B is given by the anisotropic hyperelastic Bergstrom eight-chain model which has the following Cauchy stress [52]:

$$\boldsymbol{\sigma}_B = \frac{\mu_B}{J\lambda_C}\frac{L^{-1}(\lambda_C/\lambda_L)}{L^{-1}(1/\lambda_L)}\,\mathrm{dev}[\boldsymbol{b}^*] + \kappa(J-1)\mathbf{I} + \frac{B}{\lambda_F}\left(1 - \frac{1}{\lambda_F}\right)\boldsymbol{F}\boldsymbol{e}_2 \otimes \boldsymbol{F}\boldsymbol{e}_2 \tag{5}$$

where $[\mu_B, \lambda_L, \kappa, B]$ are material parameters, J=det[**F**], $\lambda_C = (\mathrm{tr}[\mathbf{b}^*]/3)^{1/2}$ is the molecular stretch, $\mathbf{b}^*$ is the distortional left Cauchy-Green tensor, and $\lambda_F = \| \mathbf{F}\mathbf{e}_2 \|$. The rate of viscoplastic flow is given by rate of deformation tensor [54]:

$$\boldsymbol{D}_A^v = \left(\frac{\tau}{f\tau_b}\right)^m \frac{\mathrm{dev}[\boldsymbol{\sigma}_A]}{\tau} \tag{6}$$

where τ is the Frobenius norm of the stress $\boldsymbol{\sigma}_B$, and f is the exponential yield evolution function: $f = f_f + (1\text{-}f_f)\exp(\text{-}\varepsilon_v/\varepsilon_h)$, and $[\tau_b, m, f_f, \varepsilon_h]$ are material parameters. As discussed by Eswaran [52], this model framework was able to capture the stress-strain response of PLLA at different strain rates and orientations, and passed validation testing of ring tension

experiments.

CONCLUSIONS

Polylactide (PLA) and other bioresorbable polymers play an increasingly important role in many kinds of medical devices, including stents and orthopedic implants. The understanding of how to tailor the mechanical response of this important class of materials is now starting to emerge, and the use of PLLA and PLA blends will continue to grow. Despite the advances in process optimization and microstructural characterization, there is still a lack of understanding of how the microstructure controls the magnitude of anistropic viscoplastic flow, and how the microstructure can be controlled through manufacturing and heat treatments.

One of the unique features of bioresorbable polymers is their ability to degrade in biomedically relevant conditions. This degradation, which is ultimately the main reason for the success for PLLA in medical devices, is controlled by the molecular weight and orientations, the degree of crystallinity, and the applied chemical and load environment.

The magnitude of experimentally observed non-linear behaviors increases the importance of computational modeling to both understand how a device will behave in a given environment, and to optimize the device for a given application. A number of carefully developed constitutive models are now available for predicting the material response in different load environments. These models, if applied properly, can provide great insight into the response of various materials and designs. Due to the high interest in this area from both academia and industry, we can only expect computational modeling to become ever more powerful in the coming years.

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Table 1. Common bioresorbable polymers for biomedical applications.

Material	**Description**
PLA, poly(lactide)	Polylactide (PLA), also called poly(lactide), is an aliphatic polymer that exists as two stereoisomers: poly (L-lactide) (PLLA) and poly (D-lactide) (PDLA).
PLLA, poly(L-lactide)	PLA homopolymer that is typically semi-crystalline. Has the slowest degradation rate of all PLA materials due to its high crystallinity. Can be made amorphous by rapid quenching after molding.
PDLA, poly(D-lactide)	PLA homopolymer that is typically semi-crystalline.
PDLLA, poly(DL-lactide)	Copolymer of PLLA and PDLA. Amorphous if more than 15% of the D-anantiomer [23] [36]. Normally consists of random copolymers of L and D-lactide in equimolar amounts (racemic state) [36] [55] [33] [1]
PLDLLA, poly(L,DL-lactide)	Blend of stereoregular PLLA and recemic PDLLA.
PGA, poly(glycolide)	Simplest linear alphatic polyester. Often used copolymerized with PLA and PCL.
PLGA, poly(L-co-glycolide)	Copolymer of PLA and PGA. Most commonly used drug-eluting layer for delivery of pharmacalogical agents that help inhibit restenosis [56] [34]
PCL, poly(ε-caprolactone)	Exhibit rubbery characteristics [57]. Commonly used as a copolymer with PLA.

Table 2. Comparison between different material model frameworks for PLA modeling.

Model	**Class**	**Degradation Included**	**Visco-plastic effects**	**Anisotropic effects**	**Used in FEA**
Soares [39]	Hypelelastic	Yes	No	No	Yes
Hayman [21]	Hyperelastic	Yes	No	No	Yes
Kahn [49]	Linear Viscoelatic	Yes	No	No	Yes
Söntjens [36]	Viscoplastic	Yes	Yes	No	No*
Eswaran [52]	Viscoplastic	No	Yes	Yes	Yes

*It is not clear from available publications if the authors have implemented the material model into a finite element user-material.

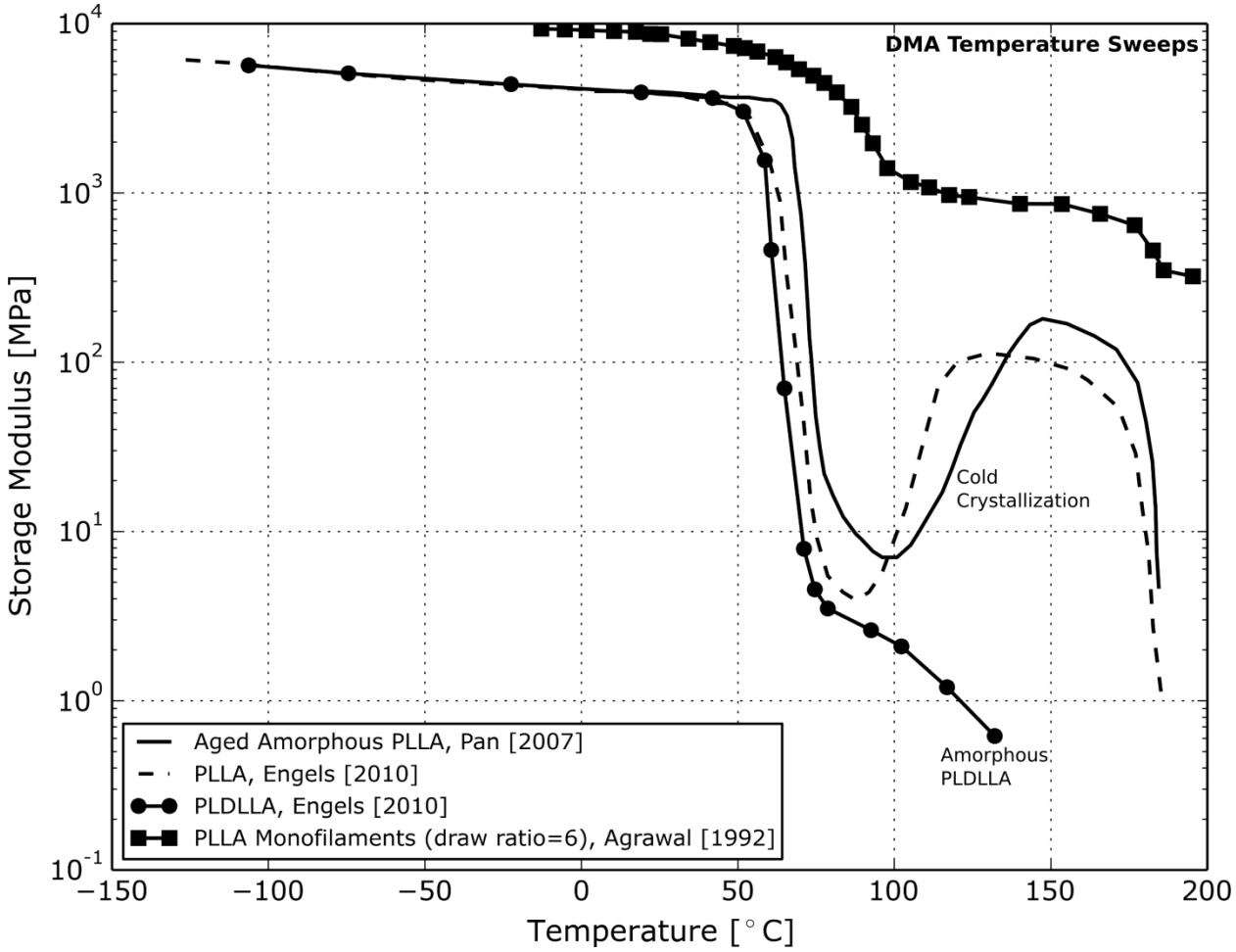

Figure 1. Storage modulus of PLLA monofilaments as a function of temperature and draw ratio. The materials characterized by Pan [26] and Engels [28] have a draw ratio of 4 while the materials characterized by Agrawal [25] have a draw ratio of 6.

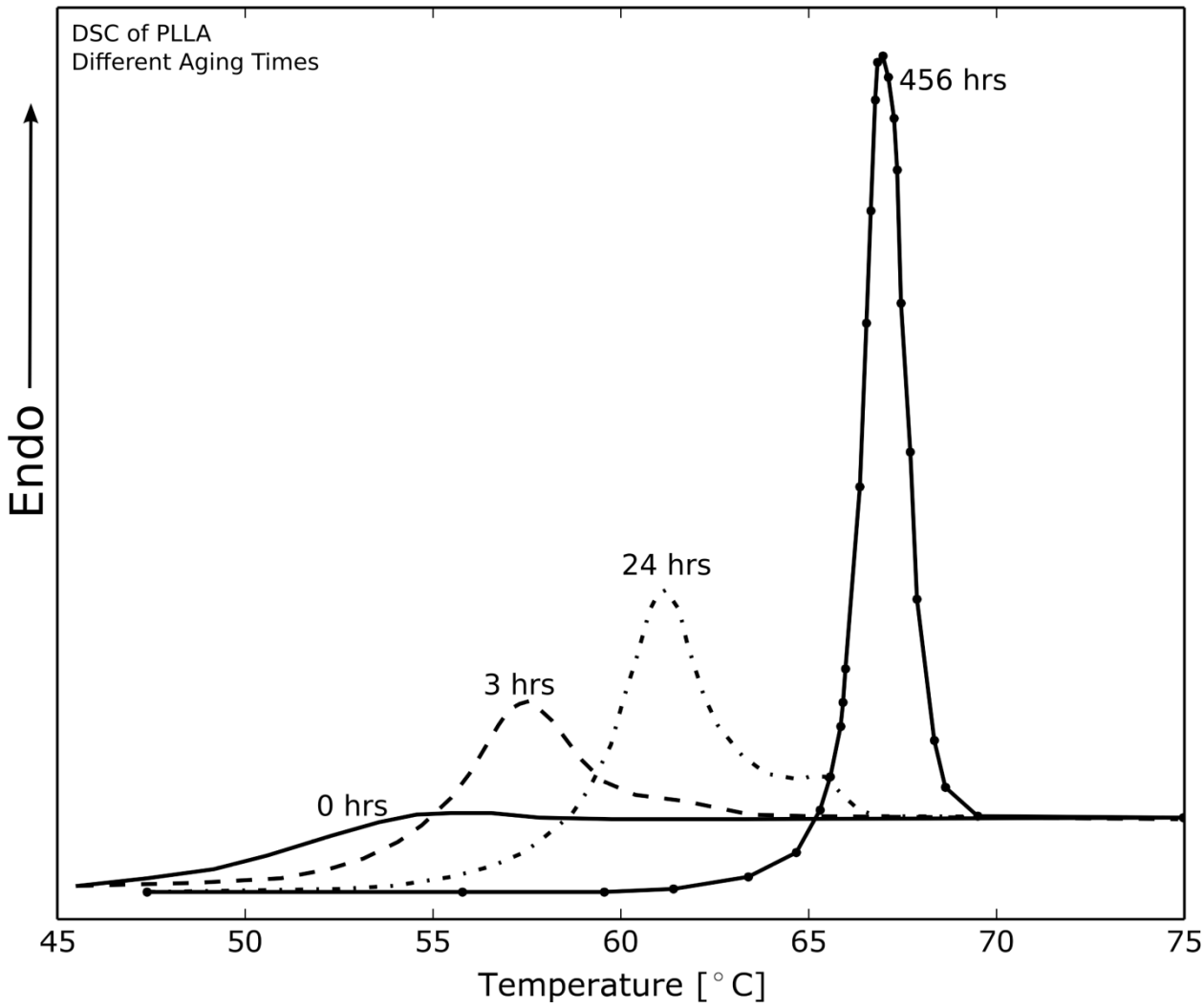

Figure 2. DSC heating scans of PLLA(10°C/min). The curves in the figure are for different aging times at 40°C [26]. The presence of endothermic peaks and shift in the endotherms to higher temperatures is correlated to the degree of physical ageing.

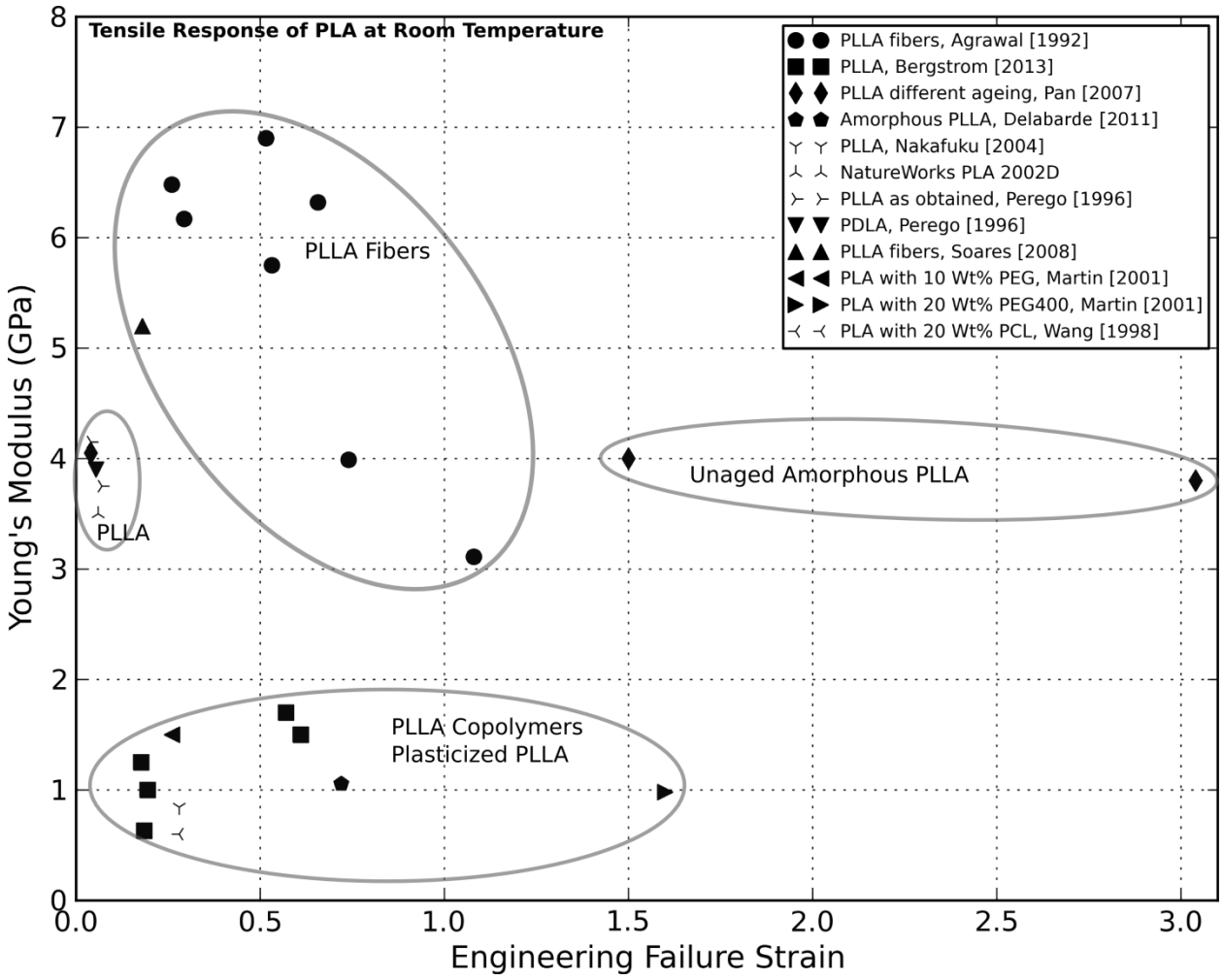

Figure 3. Young's modulus and engineering strain to failure for different PLA materials. The data are from the following references: [25] [32] [26] [33] [56] [55] [45] [31] [57].

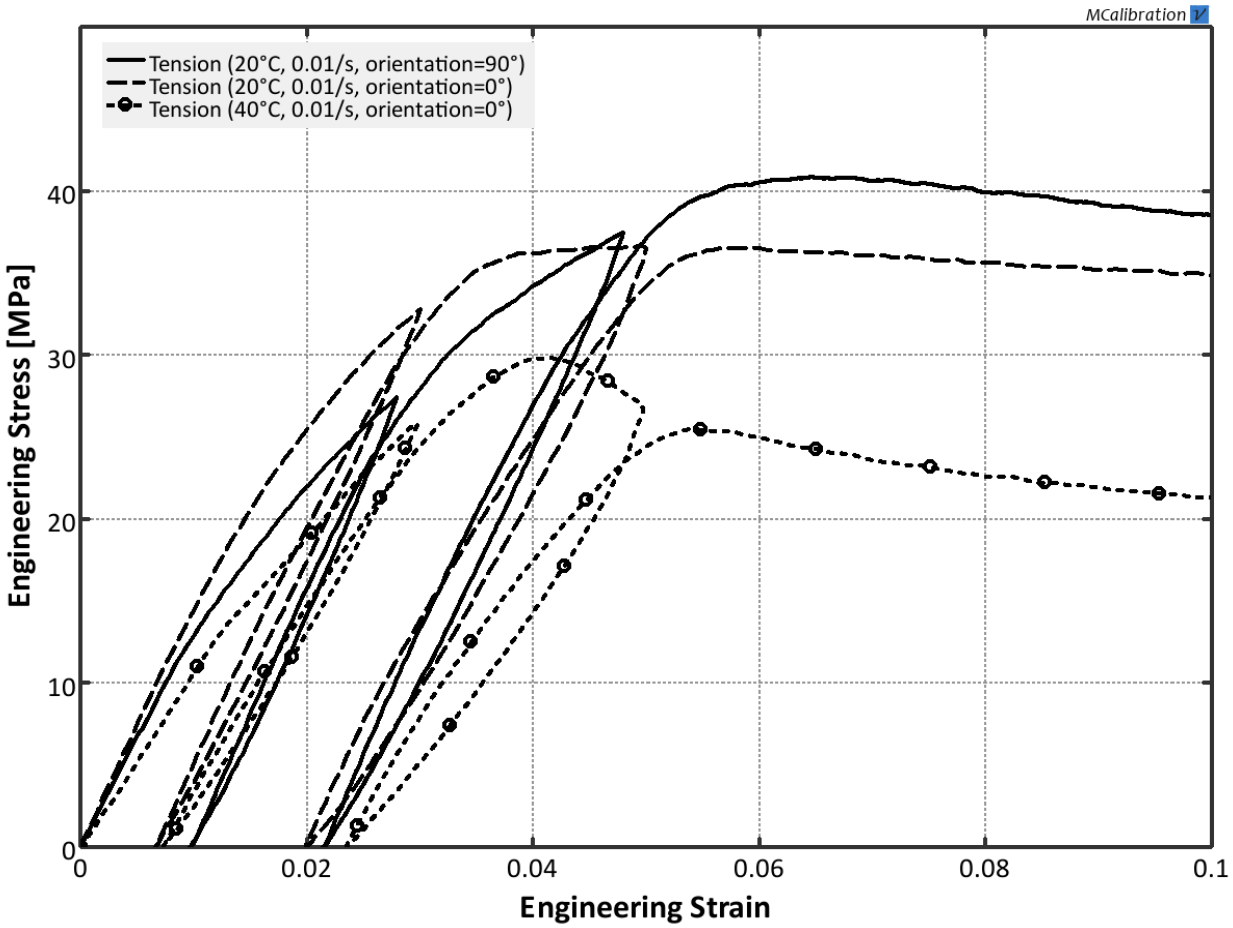

Figure 4. Uniaxial tensile behavior of a PLLA tested at a strain rate of 0.01/s in two orthogonal directions, and at two temperatures [32]. The material response is non-linear viscoplastic.

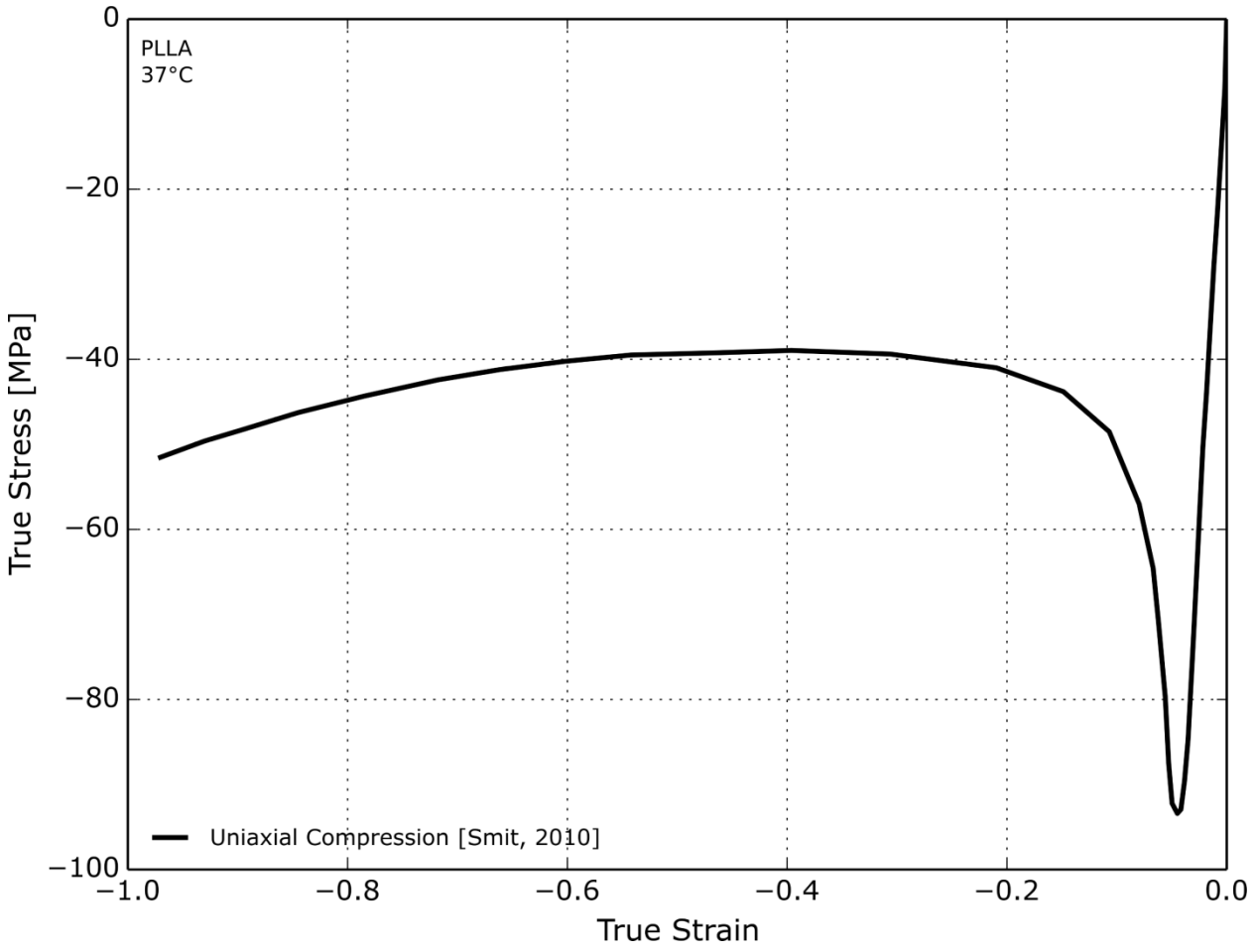

Figure 5. Experimentally determined uniaxial compressive response of a PLLA loaded at 37°C [35]. The magnitude of stress drops significantly after the yielding.

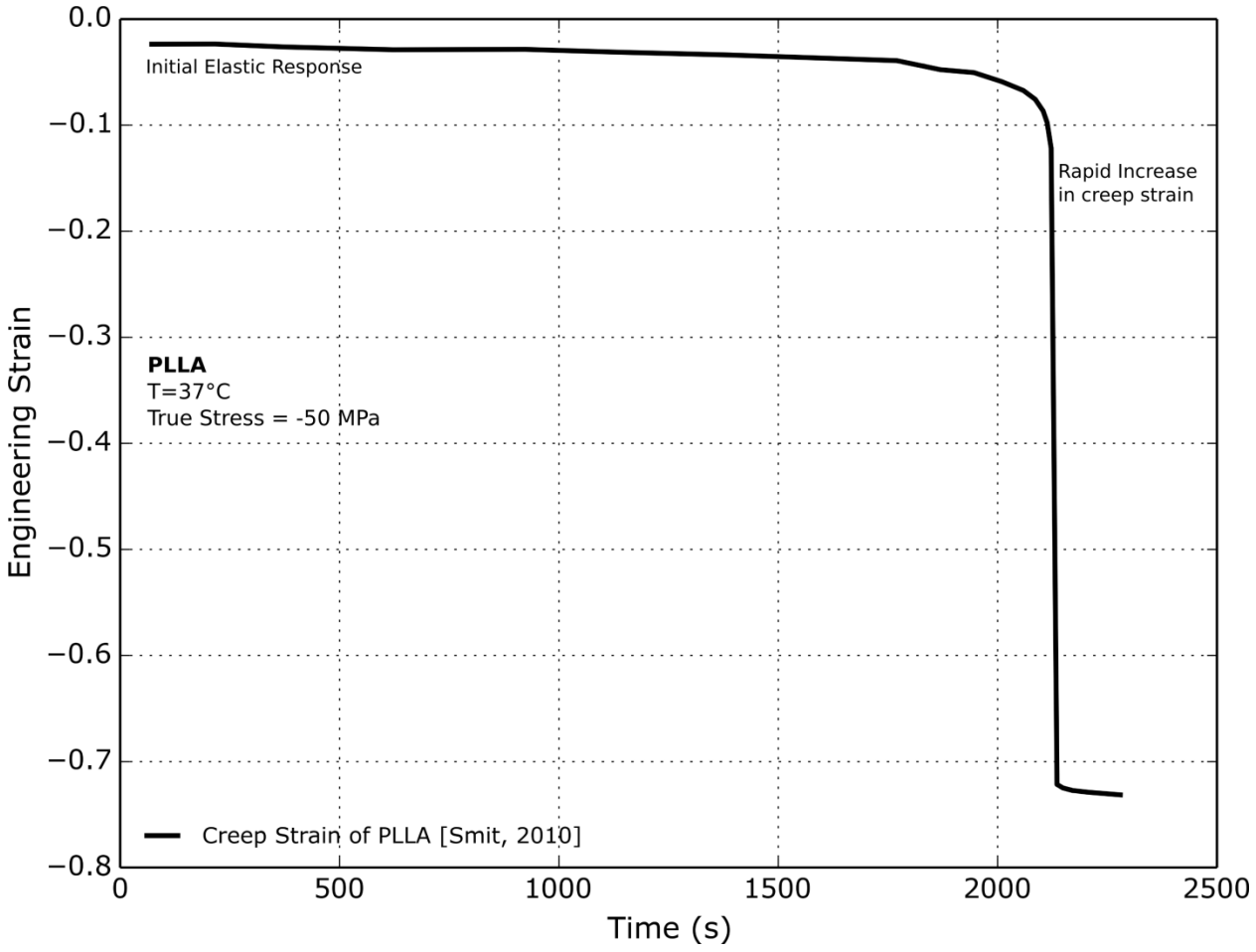

Figure 6. Creep response of a PLLA tested in uniaxial compression at -50 MPa at 37°C [35]. The creep strain increases rapidly after about 2200 seconds.