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Intrinsic Mechanical Behavior of Poly(Lactic Acids)

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Introduction
Poly(lactic acids) or PLAs are polyesters manufactured from lactic acid or the cyclic lactide. The most common stereoisomer of lactic acid, present in the human body, is the L-stereoisomer. Recently, the D-stereoisomer has also become widely available, opening the road to a variety of stereoregular and stereoirregular PLAs with different properties.

These monomers can be manufactured from renewable resources like cornstarch or sugar, and the resulting polyesters are fully biodegradable into non-toxic products. These properties make PLA an attractive alternative to conventional polymers in e.g. the package industry. The biodegradability and the lack of toxicity also make PLAs attractive materials for medical implants like sutures, (drug-eluting) stents and orthopedic implants.

Long-term Mechanical Properties
PLA implants are generally expected to last around 1 year, solely based on hydrolytic degradation kinetics. For applications where the material is under significant mechanical load, however, the lifetime can be considerably shorter due to the intrinsic mechanical deformation and failure kinetics of PLA. This means that e.g. orthopedic implants may fail considerably faster than based on degradation alone. The kinetics of deformation and failure can be described with:

\[ \tau_{\text{pl}} = \tau_0 \exp \left( \frac{-\Delta U}{RT} \right) \sinh \left( \frac{\sigma \nu^*}{RT} \right) \]

These monomers lead to marked differences in thermal and mechanical properties. The deformation kinetics depicted above are very similar for both materials. The semi-crystalline PLLA is a semicrystalline material, whereas the PLDLLA is fully amorphous. In the DMTA traces there both materials show an α-transition around +50ºC and a β-transition around −50ºC. The crystallinity of the PLLA material leads to a more extended rubber plateau.

The DSC traces shows that the stereoregular PLLA is a semicrystalline material, whereas the PLDLLA is fully amorphous. In the DMTA traces there both materials show an α-transition around +50ºC and a β-transition around −50ºC. The crystallinity of the PLLA material leads to a more extended rubber plateau.

The deformation kinetics depicted above are very similar for both materials. The semi-crystalline PLLA, however, shows consistently higher yield stresses compared to the amorphous PLDLLA. The differences in morphology apparently also lead to a much lower critical strain value for the semi-crystalline PLLA. The activation energies for both materials are similar.

The activation volumes determined from the strain rate dependence are similar at 800 and 820 Å³. This leads to a slope of approximately 11 MPa per decade for both applied strain rate and time to failure experiments. This high slope leads to rapid failure of PLA constructs, even at moderate loads. The time to failure plots illustrate this, showing a lifetime of only 10⁶ seconds or 12 days at a moderate load of 20 MPa.

Conclusions
Changing the stereoregularity of polylactic acids by changing the stereochemistry of the monomers leads to marked differences in thermal and mechanical properties. The plastic deformation and failure kinetics, however, are not greatly affected. Because of the "fast" plastic deformation and failure under load, PLAs are not a favorable construction material for a construct in a stressed environment.

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