VISCOELASTIC PROPERTIES OF AMORPHOUS POLYMERS

Graph showing:
- Glassy region
- Rubbery plateau
- Cross-linked elastomers
- Low molecular weight
- Melt

Measured over some arbitrary time period - say 10 secs
TIME TEMPERATURE EQUIVALENCE

Stretch sample an arbitrary amount, then measure the stress required to maintain this strain. Then \( E(t) \sigma(t)/\varepsilon_0 \)
RELAXATION IN POLYMERS

First consider a hypothetical isolated chain in space, then imagine stretching this chain instantaneously so that there is a new end-to-end distance. The distribution of bond angles (trans, gauche, etc) changes to accommodate the conformations that are allowed by the new constraints on the ends. Because it takes time for bond rotations to occur, particularly when we also add in the viscous forces due to neighbours, we say the chain RELAXES to the new state and the relaxation is described by a characteristic time \( \tau \).
AMORPHOUS POLYMERS - THE FOUR REGIONS OF VISCOELASTIC BEHAVIOUR

GLASSY STATE - conformational changes severely inhibited.

Tg REGION - cooperative motions of segments now occur, but the motions are sluggish (a maximum in tan δ curves are observed in DMA experiments)

RUBBERY PLATEAU - $\tau_+$ becomes shorter, but still longer than the time scale for disentanglement

TERMINAL FLOW - the time scale for disentanglement becomes shorter and the melt becomes more fluid-like in its behaviour
SEMI-CRYSTALLINE POLYMERS

- Motion in the amorphous domains constrained by crystallites
- Motions above Tg are often more complex, often involving coupled processes in the crystalline and amorphous domains
- Less easy to generalize - polymers often have to be considered individually - see DMA data opposite

MECHANICAL AND THEORETICAL MODELS OF VISCOELASTIC BEHAVIOUR

DEFINITIONS

Relaxation modulus

\[ G(t) = \frac{\tau(t)}{\gamma_0} \]

Creep compliance

\[ J(t) = \frac{\gamma(t)}{\tau_0} \]

\[ G(t) \neq \frac{1}{J(t)} \]

GOAL - relate \( G(t) \) and \( J(t) \) to relaxation behaviour. We will only consider LINEAR MODELS ie if we double \( G(t) \) [or \( \sigma(t) \)], then \( \gamma(t) \) [or \( \varepsilon(t) \)] also increases by a factor of 2 (small loads and strains).
SIMPLE MODELS OF THE VISCOELASTIC BEHAVIOUR OF AMORPHOUS POLYMERS

Keep in mind that simple creep and recovery data for viscoelastic materials looks something like this.
While stress relaxation data look something like this.
SIMPLE MODELS OF THE VISCOELASTIC BEHAVIOUR OF AMORPHOUS POLYMERS

Extension

Hooke's law

\[ \sigma = E \varepsilon \]
SIMPLE MODELS OF THE VISCOELASTIC BEHAVIOUR OF AMORPHOUS POLYMERS

Viscous flow

\[ \tau_{xy} = \eta \dot{\gamma} \]

Newtonian fluid

Dashpot Model
STRAIN VS. TIME FOR SIMPLE MODELS

Spring

Dashpot

RESPONSE
MAXWELL MODEL

Maxwell was interested in creep and stress relaxation and developed a differential equation to describe these properties.

Maxwell started with Hooke’s law

\[ \sigma = E \varepsilon \]

Then allowed \( \sigma \) to vary with time

\[ \frac{d\sigma}{dt} = E \frac{d\varepsilon}{dt} \]

Writing for a Newtonian fluid

\[ \sigma = \eta \frac{d\varepsilon}{dt} \]

Then assuming that the rate of strain is simply a sum of these two contributions

\[ \frac{d\varepsilon}{dt} = \frac{\sigma}{\eta} + \frac{1}{E} \frac{d\sigma}{dt} \]
MAXWELL MODEL - creep and recovery

A picture representation of Maxwell’s equation

Recall that real viscoelastic behaviour looks something like this

\[ \frac{d\varepsilon}{dt} = \frac{\sigma}{\eta} \]
MAXWELL MODEL - stress relaxation

\[ \frac{d\varepsilon}{dt} = \frac{\sigma}{\eta} + \frac{1}{E} \frac{d\sigma}{dt} \]

In a stress relaxation experiment

\[ \frac{d\varepsilon}{dt} = 0 \]

\[ \frac{d\sigma}{\sigma} = \frac{\sigma}{\eta} \, dt \]

Hence

\[ \sigma = \sigma_0 \exp\left[-\frac{t}{\tau_+}\right] \]

Where

\[ \tau_+ = \frac{\eta}{E} \]

Relaxation time
MAXWELL MODEL - stress relaxation

Maxwell model

Glassy region
Transition
Rubbery plateau
Low molecular weight
High molecular weight

Real data looks something like this