Analyzing & Testing

Understanding the Cure Behavior with Rheology Kinetics
How Kinexus and Kinetics Neo work together to better optimize material performance

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Agenda

Understanding the Cure Behavior with Rheology Kinetics

• Part 1 – Introduction to Rheology [Adrian Hill]
  • Brief overview of the use of rheology to directly monitor the material change during a cure reaction

• Part 2 – Introduction to Kinetics [Elena Moukhina]
  • Overview of the theory and use of Kinetics for a fuller understanding of curing profiles

• Part 3 – Case Study of a Curing System; Rheology Data, Kinetics Analysis and Predictions [Adrian Hill and Elena Moukhina]
  • An example rheological measurement on the Kinexus rheometer, imported into Kinetics Neo to investigate the changes in conditions affect the reaction kinetics
1. Introduction to Rheology

Typical Cure Measurements
Agenda

1. Basic introduction to rheology; material science measurement
2. Rheolgical terms to describe the material changes during a curing process
3. Typical rheology cure profiles
What is rheology?

**Definition:** “The science of deformation and flow”

Rheology is a basic material science for semi-solids & liquids. We measure it, as it needs to be controlled to get needed performance.

Rheology is more than just viscosity:

- Rheology is putting the material properties into context
  - Appropriate flow conditions
  - Even at “rest”
- Gives us the science & numbers to understand real material performance

**Simple Newtonian flow**

**Non-Newtonian flow**
Rheometer Principles – Oscillation Testing
Practical Measurements of Curing Reactions

• Instead of rotating on a sample, we now **oscillate back and forth**
• We typically apply a sinusoidal signal to the sample
• This is **non-destructive testing**, so can show the properties under deformation, before flow

  • From this we can predict sample properties
  • Typical variables
    • **Shear Stress, \( \sigma [\text{Pa}] \)**: force (f or p) per area (a)
    • **Strain, \( \gamma [\text{no units or \%}] \)**: displacement (u) divided by height (h)
      • (% strain is the above equation *100)

• Measures:
  • **Complex Modulus** – the stiffness of material
  • **Phase Angle** – “degree” of fluidity of the sample from 0 to 90°
  • **Complex/Dynamic Viscosity** – Cox-Merz approximation from osc
  • **Elastic (G’) and Viscous (G’”) modulus** - calculated
Disposable Plates for Curing Systems
Kinexus Disposable Plate System (KNX2155 Peltier / KNX2263 HTC)

The upper geometry stub and the lower plate are designed to be disposable (at a low price)

The upper geometry is held inside the clamp mechanism

The lower disk is held in place by the clamping ring

Geometry recognition remains with the system configured for the geometry choices
With rheology being the science of deformation and flow, it is an ideal tool to monitor a cure

- A lot of this discussion is also relevant to gelling

Typically, we are looking at changes with

- Time
- Temperature, or
- External trigger: UV/light radiation

Take this example where the sample starts off low viscosity & gets higher
Complex Modulus – G* [Pa]

From oscillation we can measure the materials complex modulus, the **stiffness of a material**

The higher the modulus the tougher the material

Calculated from how much a sample moves for a given force

Units of Pascals (Pa)

\[
\text{Modulus} = \frac{\text{Shear Stress}}{\text{Shear Strain}} = \frac{\sigma}{\gamma}
\]

Cox Merz “Rule”...

This empirical approximation can indicate a complex or dynamic viscosity from oscillation data which can be preferred:

- Complex Viscosity \(= \frac{\text{Complex modulus}}{\text{Angular frequency}}\)
- Dynamic Viscosity \(= \frac{\text{Viscous modulus}}{\text{Angular frequency}}\)

**Note**: shows the same trends
Phase Angle [°]

For a Purely Elastic Material – *Solid-like* behaviour
The stress and strain are exactly in phase
Therefore the phase angle is zero

For a Purely Viscous Material – *Liquid-like* behaviour
Stress and strain are 1/4 of a cycle out of phase
Therefore the phase angle is 90°

Phase angle can be considered a scale of “fluidity” from
0° (solid like) to 90° (liquid like)

[Tan delta is simple the tan(phase angle), with a range from
0 (solid like) to 0.5 (“gel point”/ d=45°) to infinity (liquid like) ]
Storage and Loss Modulus

- Rheology language tends to use a combined form of complex modulus and phase angle

- **Storage (elastic) modulus** $G'$
- **Loss (viscous) modulus** $G''$

- If $G' > G''$, phase angle less than 45° - **SOLID LIKE**
- If $G'' > G'$, phase angle greater than 45° - **LIQUID LIKE**

- $G^*$ - modulus is the overall stiffness of a material
Curing Example
Comparing different samples

Direct measurement of the material changes through a cure

Typically consider:
- Complex modulus, or
- Complex viscosity, or
- Dynamic viscosity
- Elastic/viscous modulus
- Phase angle or tan delta
2. **Introduction to Kinetics Neo**
Understanding the cure behavior with rheology kinetics
Agenda

1. What is chemical kinetics?
2. Example of curing data, kinetics analysis and predictions
What does chemical kinetics study?

**Chemical Kinetics** answers the following questions:

- How fast is the reaction?
- What is the reaction mechanism?
- What is mathematical model of chemical process

Reaction rate depends on:
- Temperature
- Concentration
- Pressure
- Catalyst,
- Solvent
- ...

NETZSCH Kinetics Neo software
Main problem: how to reduce the costs?

Ceramics production: What is optimal firing temperature profile?

Problem:
- **Fast** firing: **cracks** and deformations
- **Slow** firing: too **expensive** production process

Laboratory measurements + Kinetic analysis + process optimization:
Production time was reduced more than by 50% from WEEKS to DAYS

New material
HALFOAM ALUMINA™
Curing, cross-linking

- What happens during curing? How high is the reactivity?
- At which temperature and time curing starts and finished?
- What is the optimum curing process (time/temperature)?
- How high is the degree of curing?
- Where is the glass transition temperature?
- How to reduce costs during production?
- What is the final state of the epoxy after given time at given temperature? (glass /elastic solid/viscose liquid)
Steps to solve Kinetic Tasks in Kinetics Neo

**Measured raw data**
- File 1
- File 2
- File 3
- File 4

**Data Import and Processing**
- Processed File 1
- Processed File 2
- Processed File 3
- Processed File 4

**Kinetic Model**
- Autocatalytic (Cn)
- Reaction of n-th order
- Kamal-Sourour
- Friedman
- Ozawa

**Simulations**
- Predictions: isothermal / dynamic / arbitrary
- Predictions: degree of cure / curing rate / viscosity
- Optimization: conversion rate
- Optimization: curing profile
Cure Monitoring: Rheometry

![Image of rheometer and temperature sensor](image)

![Graph showing temperature sweep with G', G'', and tan δ](graph)

- G''
- G'
- tan δ

Temperature (°C)

Graph axis labels:
- G' (Pa)
- G'' (Pa)
- tan δ

Graph scale:
- 10^0 to 10^14
Parts of Measured Viscosity Signal

Viscosity for materials **without curing**

Viscosity change **because of curing**

Viscosity (total signal)
Target: find degree of curing from the imported data

Steps:
1. Select evaluation range
2. Switch to Temperature scale
3. Remove Viscosity(Temperature) without curing
4. Recalculate to conversion
Curing can be described by the equation \( C_n \) for autocatalytic reaction:

\[
\frac{d\alpha}{dt} = A \cdot (1 - \alpha)^n \cdot (1 + K \alpha^m) \cdot \exp\left(\frac{-E_a}{RT}\right)
\]

This equation with its parameters \( A, E_a, K, m, n \), is the kinetic model.

Kinetic parameters are found from the best fit for all experimental data.
Kinetic Model: Single-Step Autocatalytic Reaction of Cn type
Predictions 1
What is viscosity for user-defined temperature program?

Constant heating: measured reaction rate

New temperature program: Unknown viscosity

No new measurement
Calculation with Kinetics Neo
Predictions 2
What is degree of cure for user-defined temperature program?

Constant heating: measured reaction rate

New temperature program: Unknown degree of cure

No new measurement
Calculation with Kinetics Neo
NETZSCH Kinetics Neo Web Site including User Guides
https://kinetics.netzsch.com

Gelation Curve
12. If the conversion for gelation point is known then gelation curve can be shown. Let us show gelation curve for known conversion value 52%.

Write 1°C for temperature step and sum up Glass transition Temperature Tg.
Press Calculate.
For Isocconversion Lines click "Mono", then Custom and select one value 0.52.
Conclusion

Kinetics Neo Software help to do:

1. Calculation of one mathematical kinetic model for several measurements
2. Prediction of degree of cure for the new temperature profile
3. Prediction of viscosity for new temperature profile
4. Prediction and glass transition temperatures (temporary DSC only)
5. Optimization of curing process. Find the concentrations in order to have what we want to have
3. Case Study of a Curing System
Rheology Data, Kinetics Analysis and Predictions
Curing example: ARALDITE

2-component adhesive

“Very fast setting”: 5 minutes…

Complete curing 24 hours
Kinexus Measurements

Araldite measured at two different temperature ramps

Same data presented in different ways

- Complex modulus
- Phase angle
- Temperature

Complex viscosity

Temperature

- $5^\circ C/min$
- $2^\circ C/min$

- Complex modulus
- Phase angle
- Temperature
ARALDITE, Rheometry measurements

Temperature program consists of
1. Heating
2. Isotherm
3. Cooling

Measured data:
1. shear stress (*)
2. shear strain (*)
3. shear modulus (elastic component) $G'$
4. shear modulus (viscose component) $G''$
5. shear modulus (complex component (*)
6. shear viscosity (complex component) (*)
7. $\tan(\Delta)$

(*) not shown on the graph

Gel point

First step

Second step $T_g=30^\circ C$
1. DSC measurements contain 2 peaks
   First peak is 49.7°C
   Second peak is 118.6°C

2. Glass transition
   for uncured material: -25.5°C
   for totally cured material 30.1°C

   This is in agreement with Tg from Rheometric measurement
ARALDITE, Rheometry measurements for kinetic analysis

Source Data

Legend
- 2K_min.csv, log(Visc.)
- 2K_min.csv, Temp.
- 5K_min.csv, log(Visc.)
- 5K_min.csv, Temp.

Time / min

Temperature / °C

log(Visc.) / (Pa*s)

-5
-3
-1
0
1
3
5
7
9

5 K/min

2 K/min

10
20
30
40
50
60
70

0
100
150
200
250

2 K/min

5 K/min

10^17
10^16
10^15
10^14
10^13
10^12
10^11
10^10
10^9
10^8
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
20
40
60
80
100
120

Temperature sweep

2 K/min

5 K/min
Two-step kinetic model can describe raw measurements, conversion and conversion rate. Fit quality $R^2=0.999$
Prediction of conversion and viscosity for complex temperature program

<table>
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<th>End T/°C</th>
<th>H.R./K/min</th>
<th>Time/min</th>
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5. **Kinetics Neo and Kinexus; Curing Partners**

Concluding remarks
Concluding remarks
Material analysis and kinetic analysis to give the bigger picture

Disposable Plate Systems available for rheometers to enable to monitoring of curing systems

The rheology of curing systems is a demanding test, which is usually carried out with a single frequency oscillation

Curing / gelling reactions can be analyses over time, temperature and/or UV exposure

There are several key rheological features such as minimum viscosity, gel point and final cure that can be determined to assist with QC testing and development of these systems

Kinetic analysis takes rheology data and enables reaction profiles to be understood over many conditions

Kinetics Neo creates one mathematical kinetic model for several measurements

Kinetics Neo uses this model for simulation of viscosity and degree of cure for the new user-defined temperature profile

Kinetics Neo helps to optimization the temperatures and times of curing process.
Thank you for your attention.
Any questions?
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https://kinetics.netzsch.com/