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Simulation of long term cable ageing at elevated temperature

Problems. Limitations

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Simulation of long term ageing

Operation: Cable 40 – 60 years at 60 – 90°C.

Simulation: Bring the cable to the same end condition as after long term operation, but within a reasonable time, max. some months

Need to accelerate the thermal ageing. Usually at elevated temperature.

How long at different temperatures to reach the same end-point

Must be known time to equivalent damage at different temperatures.

Normal operation, time t2 40 years

A → C T_2 60 °C

Time t1 x days

A → C T_1 110 °C

Reaction kinetic (ageing = chemical reaction)

Very roughly, you can imagine
A cable insulation
B oxygen
C degradation product
D low molecular product, e.g. methane

$$aA + bB = cC + dD$$

The rate of this reaction (r) is given by the rate of the initial material consumption (concentration decrease of original material)

$$r = -\frac{1}{a} \cdot \frac{[A]}{dt} = k_n [A]^p \cdot [B]^q$$

$p + q$: reaction order
k_n : rate constant

Note: Production of the reaction products (C, D) usually has no influence on reaction rate!! It is not evaluated

$$aA + bB = cC + dD$$

Chemical reactions (material ageing):

- What does it react and how does it react
- How fast is the reaction.

  In "ageing terminology" how long it takes to reach a specific condition
- How fast is the chemical reaction at different temperatures

Arrhenius, 1889, Sucrose hydrolysis

Sucrose + H_2O = Glucose + Fructose

$$\frac{\ln k}{dT} = \frac{E_A}{RT^2}$$

Parameter E_A is temperature independent.
The equation integrated to well known form:

$$k = A \cdot e^{\frac{-E_A}{RT}}$$

k – rate constant [depends on reaction order]
A - preexponential factor [same as k]
E_A - (Arrhenius) activation energy [J/mol]
R - gas constant [8,314 $JK^{-1}mol^{-1}$]
T - temperature [K]

- **Same reaction** at 2 different temperatures T_1 (e.g. 120 °C) and T_2 (operation 60 °C) with two different rates k_1 and k_2.
- At normal operation temperature T_2 it takes time t_2 (e.g. 40 years) to reach a specific degradation point
- At elevated temperature T_1 it takes time t_1 to reach the **same** degradation point
- E_A and A are the same at both temperatures

$$k = A \cdot e^{\frac{-E_A}{RT}}$$

$$k = \frac{dc}{dt}$$

$$\longrightarrow$$

$$t_1 = t_2 \cdot e^{\frac{E_A(T_2 - T_1)}{k_B T_1 T_2}}$$

Accelerated thermal ageing.

Arrhenius approach

$$t_1 = t_2 \cdot e^{\frac{E_A(T_2 - T_1)}{k_B T_1 T_2}}$$

$$t_s / t_a = e^{(\Phi/k)\left[1/T_s - 1/T_a\right]}$$

$$DT = \frac{DV}{e^{-\frac{Ea}{K}\cdot\left(\frac{1}{T2}-\frac{1}{T1}\right)}}$$

Time

temperature

activation energy

constants

Example

Operation: t2 = 40 years, T2 = 60°C, Ageing: T1 = 105°C

Time of ageing: t1 = 115 days, EA = 1.17 eV

t1 = 231 days, EA = 1.00 eV

1 eV = 96 486 J/mol

Note

- *This equation says nothing about the rate of ageing.*
- *It enables to calculate time to equivalent damage at different temperatures.*
- *It is valid only if chemical reactions are the same.*
- ***Does not depend on the process . It does not require knowledge of the chemical reaction. Only the initial and the final conditions are important.***

A ⟶ ....⟶ C

Question concerning equation

1. Is using of Arrhenius equation correct for thermal ageing simulation?

2. **Is there really the same reaction at normal operation temperature and at elevated temperature?**

3. **How sure we are with the activation energy. Same at both temperatures?**

1. Validity of Arrhenius equation?

The validity of Arrhenius equation has been proved on large variety of chemical reactions. From the degradation point of view there are e.g. chemical bonds scission, oxidative degradation, depolymerization.
Moreover, low molecular weight products (such e.g. H_2, CH_4) and they evaporation do not influence markedly ageing process and have only little influence on Arrhenius behavior.

Note: typical exception is PVC, where the reaction product HCl catalyzes further chain unzipping and has a very large effect on the reaction rate that may further complicate ageing estimates.

2. Same reaction at different temperatures?

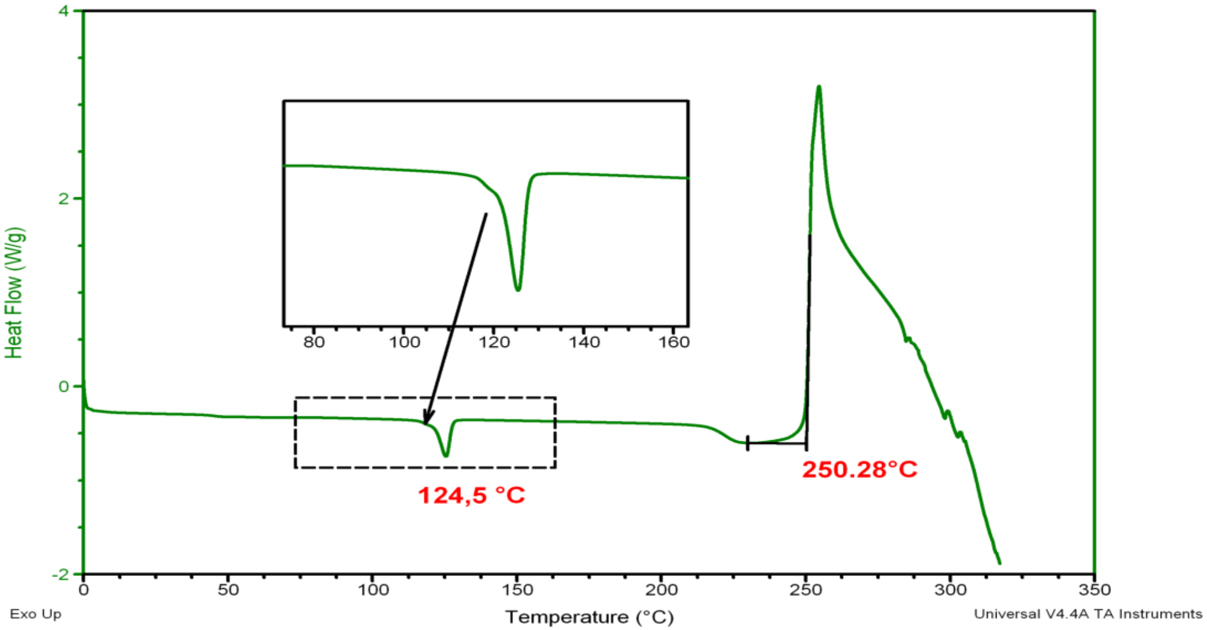
We hope, we expect, we suppose!!

Ageing simulation

Both temperatures shall be close.

Between both temperatures need not be any thermodynamic transition, chemical reaction etc.

- Range of chemical stability
- Thermodynamic transition
- Possibility of heterogeneous ageing



3. Activation energy

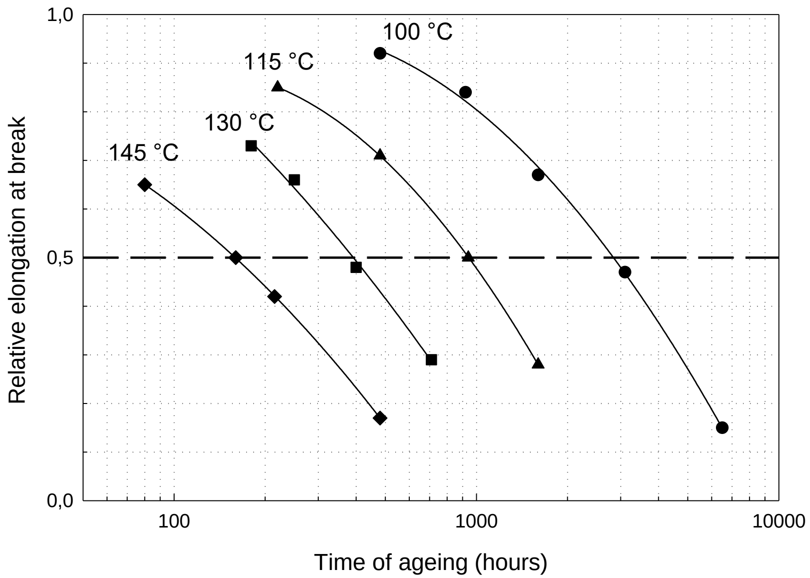
Very important factor. It influences very much the ageing process

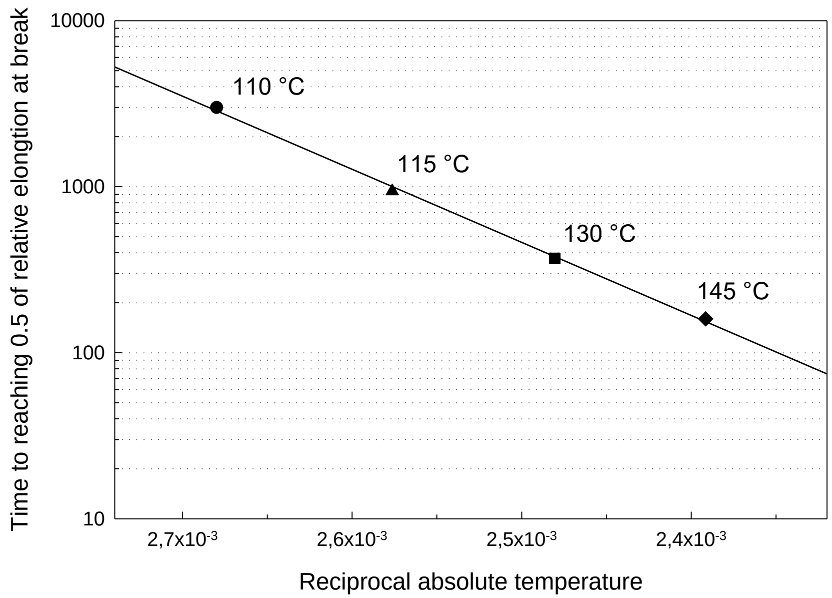
<u>Typical procedure</u>

Change of property with time at different temperatures.

Time to reach a selected value at different temperatures.

Calculate E_A from the slope of time vs. temperature





3. Activation energy

Some approximations and simplifications are used. They may influence results.

Rate constant depends on the change of concentration of initial material. At best, concentration change shall be evaluated. Normally not possible. Therefore, selected property is evaluated. **Property should be related to the concentration change** (*correlated with a particular degree of molecular change in the initial material*).

Do not evaluate products, like e.g. gas evaluation, pressure increase etc.

The **rate of any property change** with time is strongly influenced by the specific reaction and by material conversion.

E.g. color may change much faster than EtB.

OIT depends on the concentration of antioxidants

EtB depends on the degradation of polymer chain

Rates of properties changes are different.
Activation energy determined from different properties may differ.

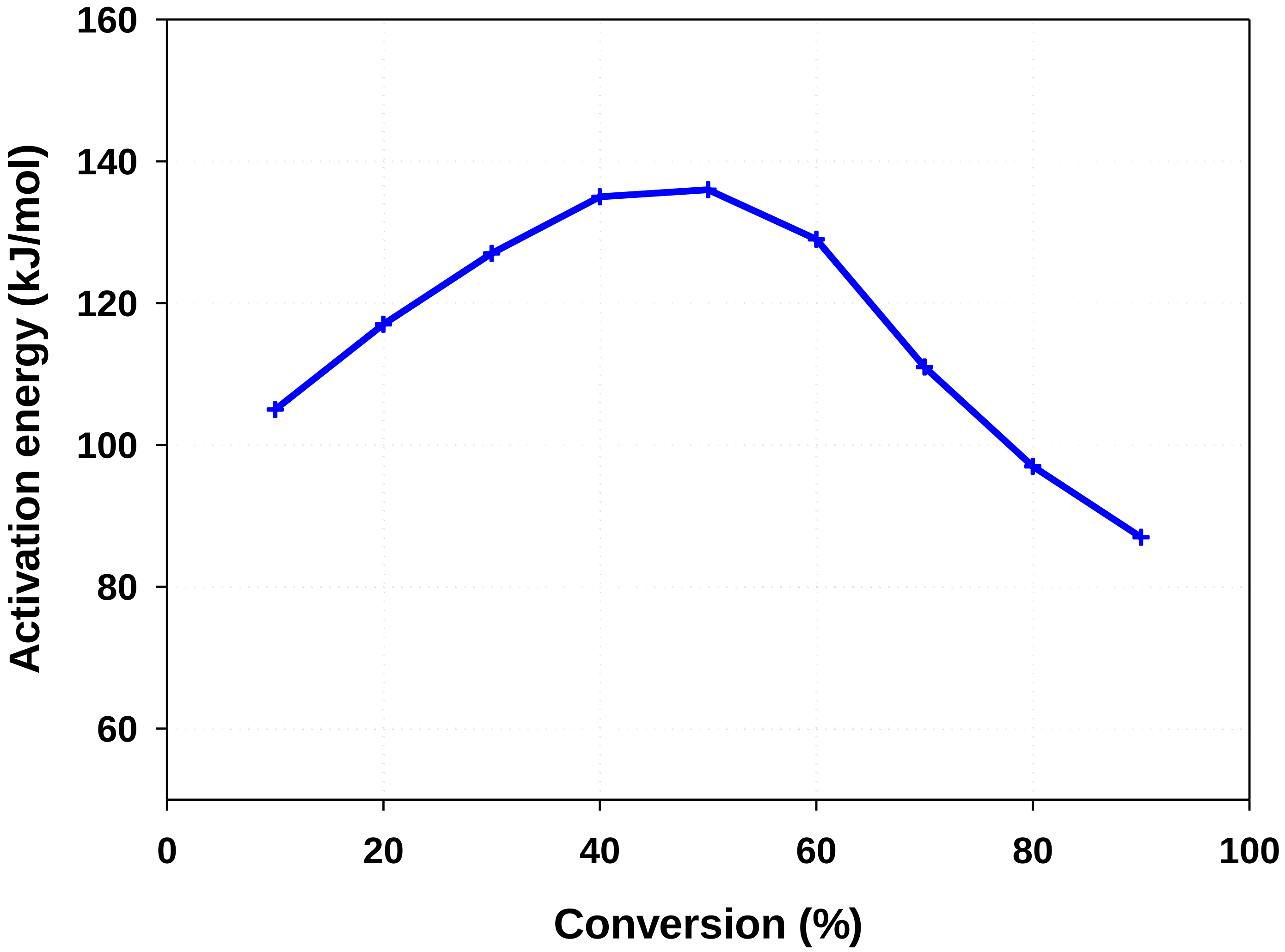
Why?

The degradation process of commercial polymers is usually:

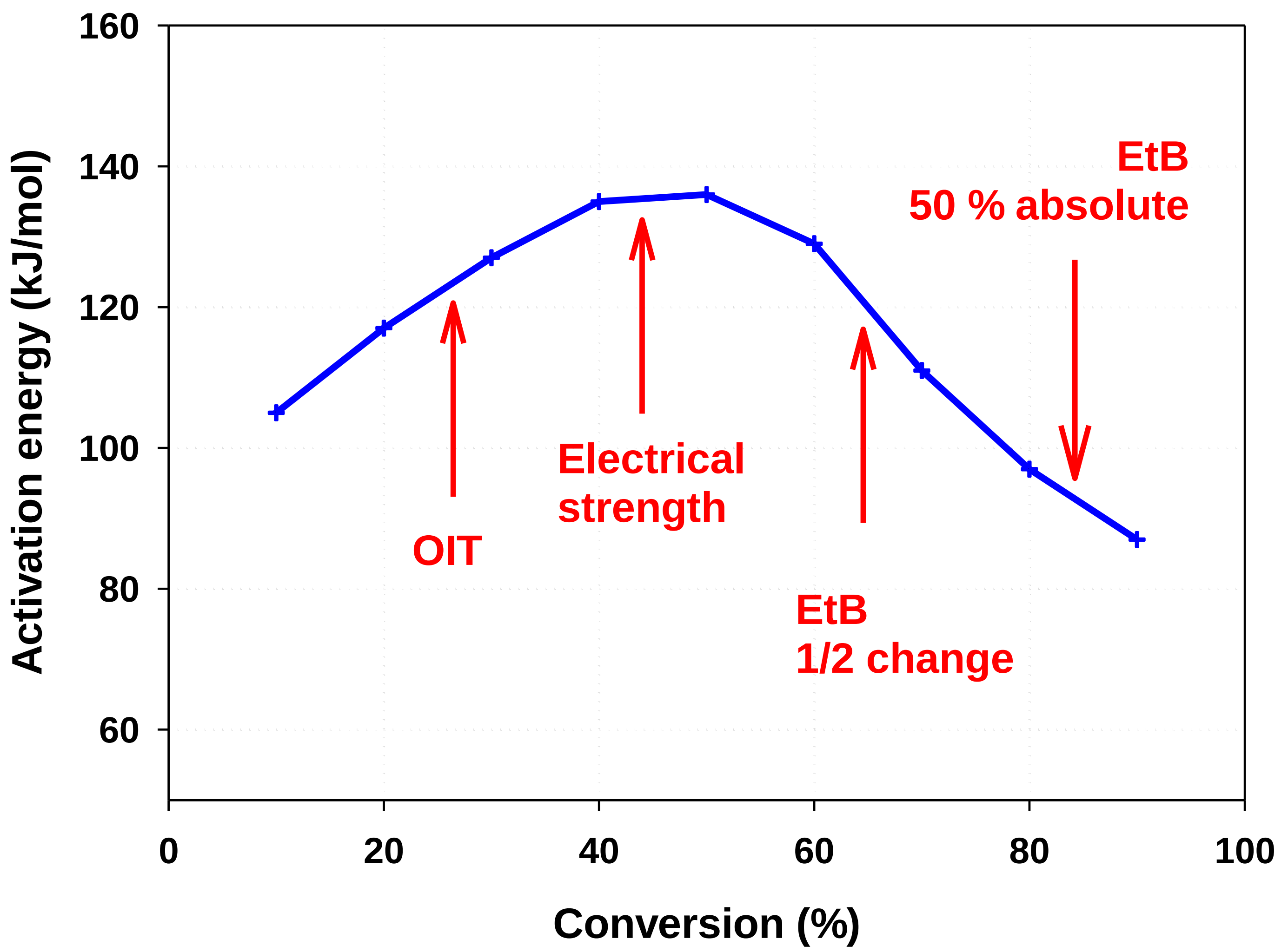
- A sum of several multistage, overlapped reactions
- That involve several compounds in the material - antioxidants, stabilizers, fillers, pigments, catalysts etc.;
- These reactions have several different activation energies.
- Besides, the chemical reactions of solid polymers are often complicated by physical processes (diffusion, sublimation, adsorption – desorption, etc.), which are also characterized by their own activation energies.
- The relative contributions of these individual steps to the overall reaction rate tend to vary with temperature and extent of conversion.

Activation energy is not constant

Activation energy may change during the ageing.



EXAMPLE



160
140
120
100
80
60
Activation energy (kJ/mol)
0
20
40
60
80
100
Conversion (%)
EtB
50 % absolute
Electrical
strength
OIT
EtB
1/2 change

Important to remember

Activation energy need not be constant during the ageing

Arrhenius approach requires single value of activation energy

Arrhenius approach expects, that the activation energy determined for one specific point of the conversion (specific property value) is temperature independent.

Conclusions

To simulate long term operation, equipment is subjected to thermal ageing at elevated temperature. Conditions of accelerated ageing are based on Arrhenius approach.

Need to know operation conditions (time, temperature), ageing temperature, activation energy. Ageing time is calculated.

Several approximations and limitations associated with using of such a method cause, that the predicted service lifetime need not be fully justified

To overcome these limitation it is important to know all the assumptions, simplifications, sources of uncertainty and manage them.

What we should do?

- For accelerated thermal ageing use Arrhenius approach.
- Do not use too high ageing temperature.
- Take into account how activation energy was determined.
- At best use value determined from an important functional property.
- Eliminate activation energy determined from product evaluation.
- Do not forget, that activation energy can be determined with a specific accuracy. Use lower 95 % confidential level.
- Use safety margin
- On going qualification, condition monitoring, deposits, CBQ.


BINDER
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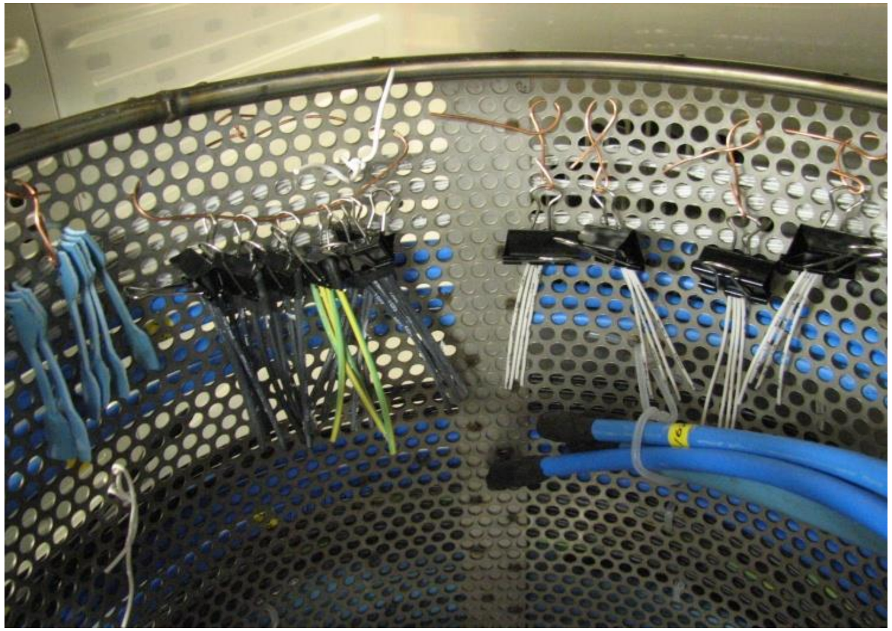

Thank you for your attention

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