

Characterization and modification of mechanical properties of hyperelastic rubber

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Mechanical properties



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Mechanical properties

Not-filled rubber has a similar modulus of elasticity K as polymer glasses. However, they differ with respect to them in several points:

- *Their Poisson ratio is close to 0.5. Consequently, the modulus E , G are much lower than K . Normal value of E non-rubber is the order of 10^0 MPa (10^{-3} GPa).*
- *The work expended on deformation of the rubber is almost completely transformed into heat.*
- *Equilibrium modulus of elasticity is proportional to absolute temperature.*

Dependence of shear stress on shear deformation of rubber is almost linear. The curve of stress on deformation in compression is nonlinear, deflected upwards. Elongation with increasing degree of cross-linking decreases monotonically, strength initially increases, reach a peak value and then decreases.

Stress increases with increasing direction in the area above the tensile curve inflection point. Length of the tensile curve inflection point and thus the value of strength and elongation is the greater the greater degree of orientation crystallization is present in the material structure.



Mechanical properties

Time (relaxation) phenomena in the range of small and medium deformations in filled natural rubber (at room temperature) are characteristic of almost negligible hysteresis. In the area above the inflection point there is observed a large hysteresis. It is caused by orientation crystallization.

- These phenomena are described by the phenomenological theory of rubbery elasticity.

Mooney-Rivlin equation (MR) is describing a tensile curve of rubbery networks very well to the inflection point.

$$\sigma_{xx} = F/A_0 = 2 C_1(\alpha - \alpha^{-2}) + 2 C_2(1 - \alpha^{-3})$$

The parameters C_1 , C_2 are evaluated from experimental data. From these equations follows the expression for elastic modulus:

$$E = 6C_1 + 6C_2; G = 2C_1 + 2C_2$$



Tensile testing

Experimental

Tested samples of EPDM and NBR rubber were present in the form of plates having dimensions of $(180 \times 160 \times 6)$ mm resp. $(180 \times 160 \times 2)$ mm. Tensile testing and biaxial tensile testing was performed on Shimadzu Autograph AG-X and 3D Optical Deformation Measurements – 3D ARAMIS.

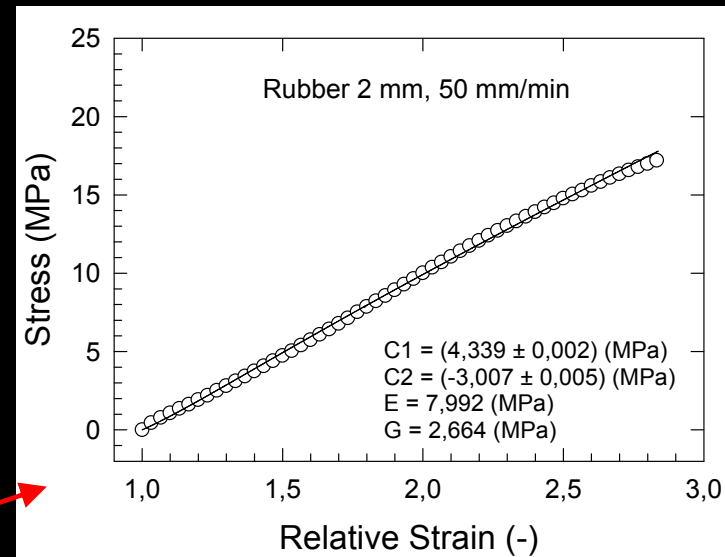
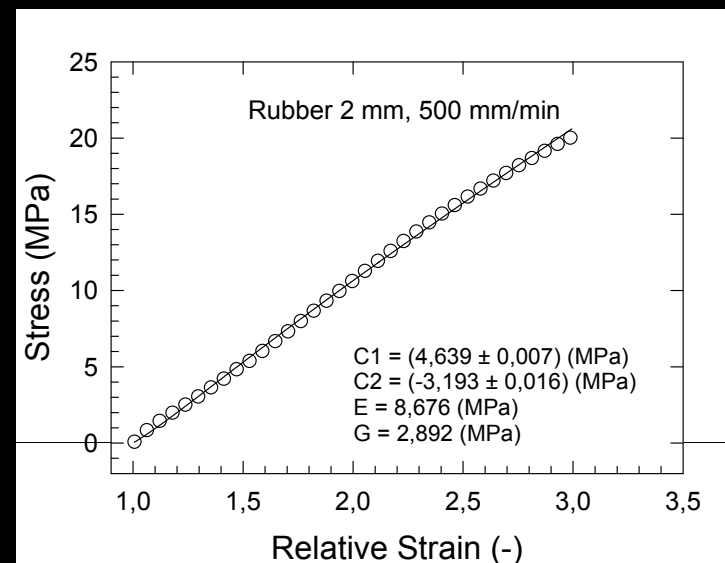
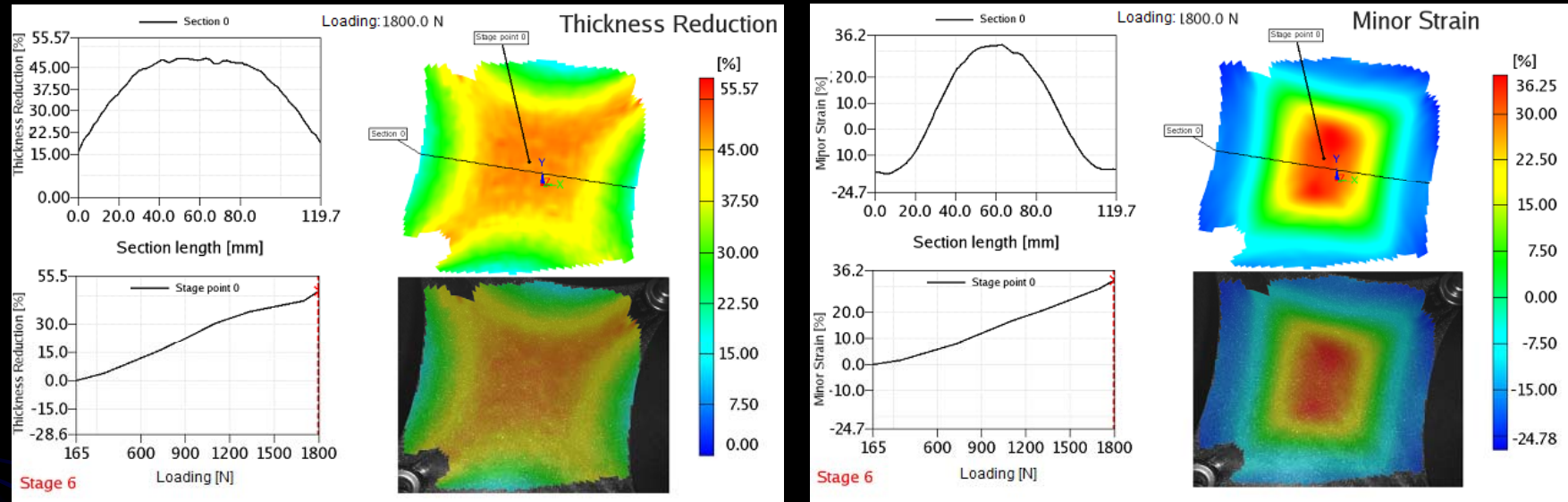


Figure: Stress strain dependence for rubber plate 2 mm thick for deformation rate 50 mm/min. Full line – results of the calculation according to the MR model.

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Bi-axial tensile testing



Figures: Bi-axial tensile testing results: (a) Thickness reduction vs. loading, (b) Minor strain vs. loading.



FEM calculations

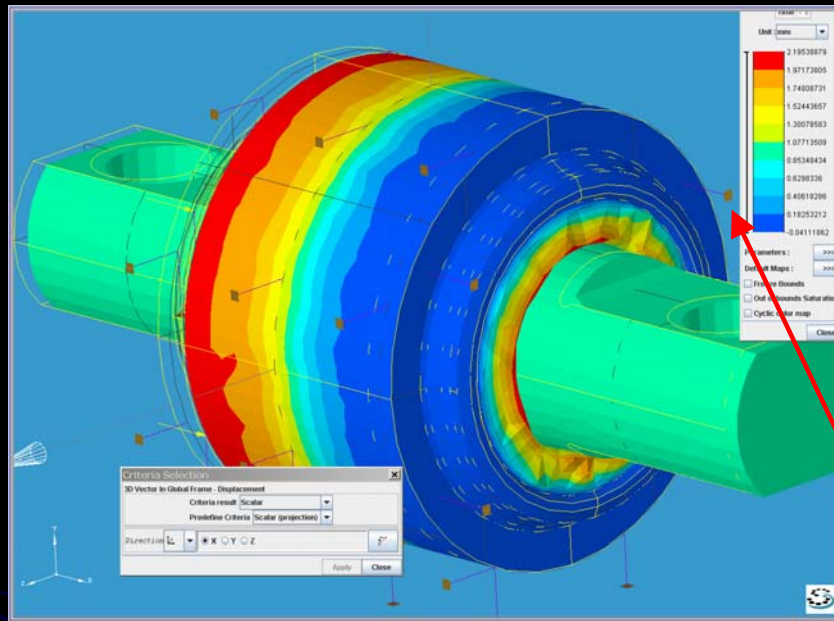


Figure: Deformation magnitude in X-axis direction.

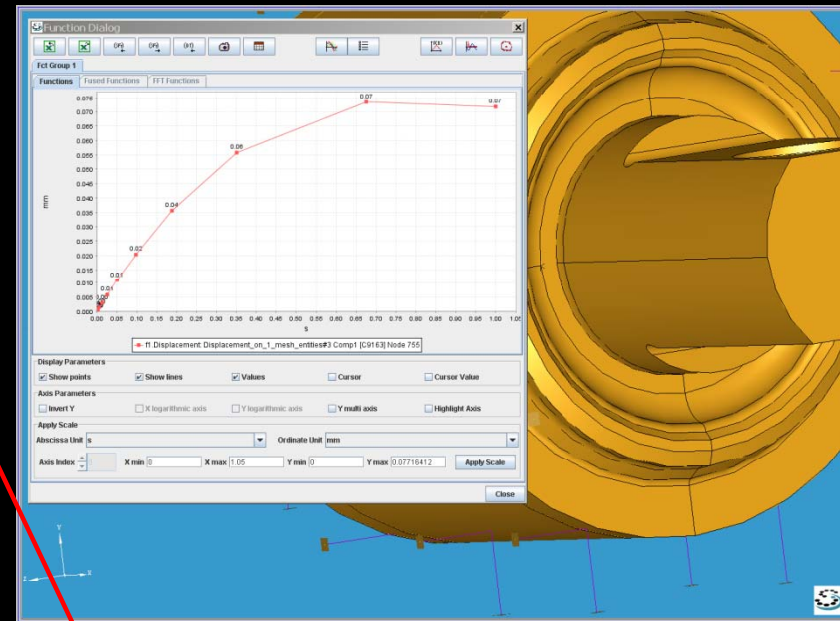


Figure: Example of non-linear deformation behavior for nod No. 755 in Z-axis direction.

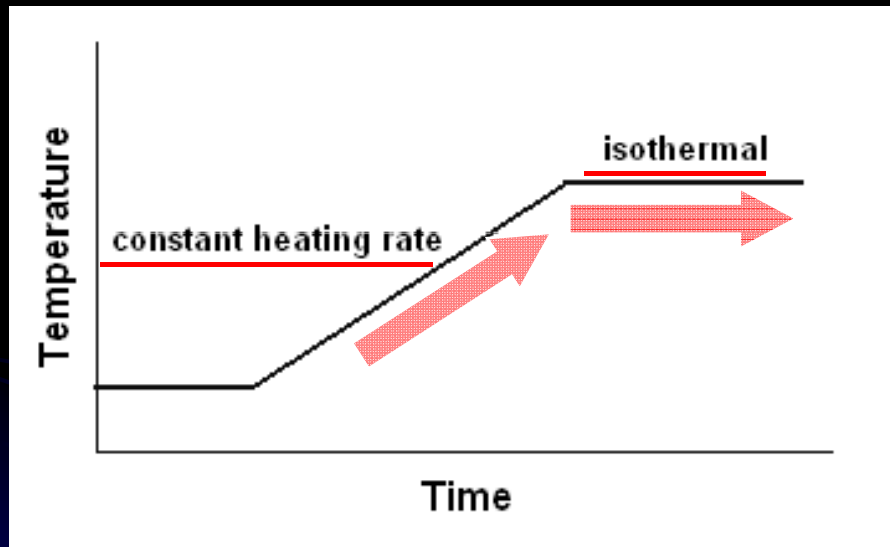


Thermal Analysis



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What is Thermal Analysis?



Thermal analysis has been defined by the International Confederation of Thermal Analysis (ICTA) as a general term which covers a variety of techniques that record the physical and chemical changes occurring in a substance as a function of temperature.



Application of Thermal Analysis Methods in Materials Science



- Organic compounds
- Inorganic compounds
- Pharmaceuticals
- Petrochemicals Plastics
- Plastics
- Foodstuffs
- Materials

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Material Properties

Nature Product
Origin
Composition
Mixture

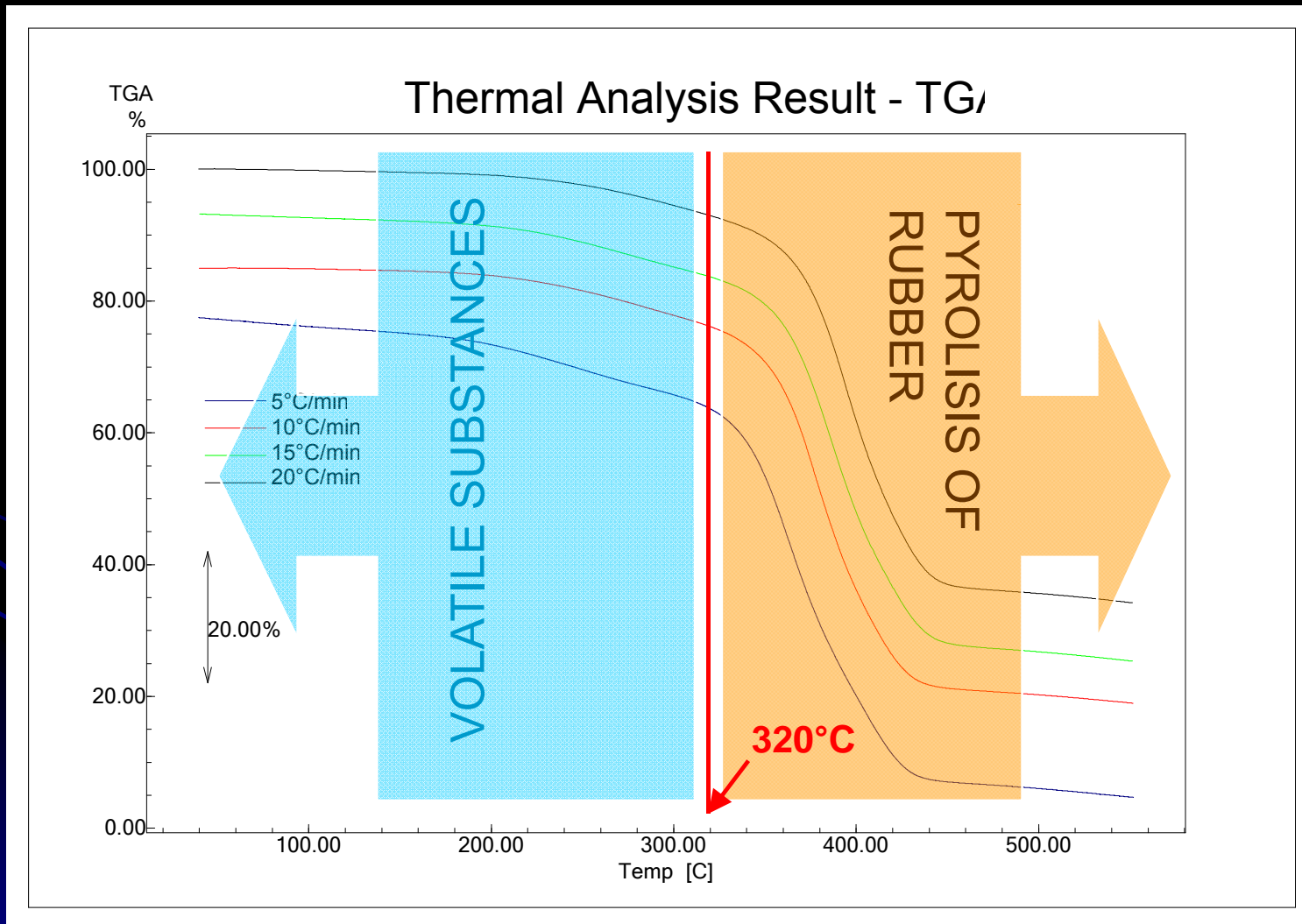
Material Properties

Aditives
Excipients
Catalysts
Plasticizer
Antioxidants
Impurities
Fillers

Processing
Thermal treatment
Mechanical stressing
Storage and use



Thermogravimetry analysis of hyper elastic rubber

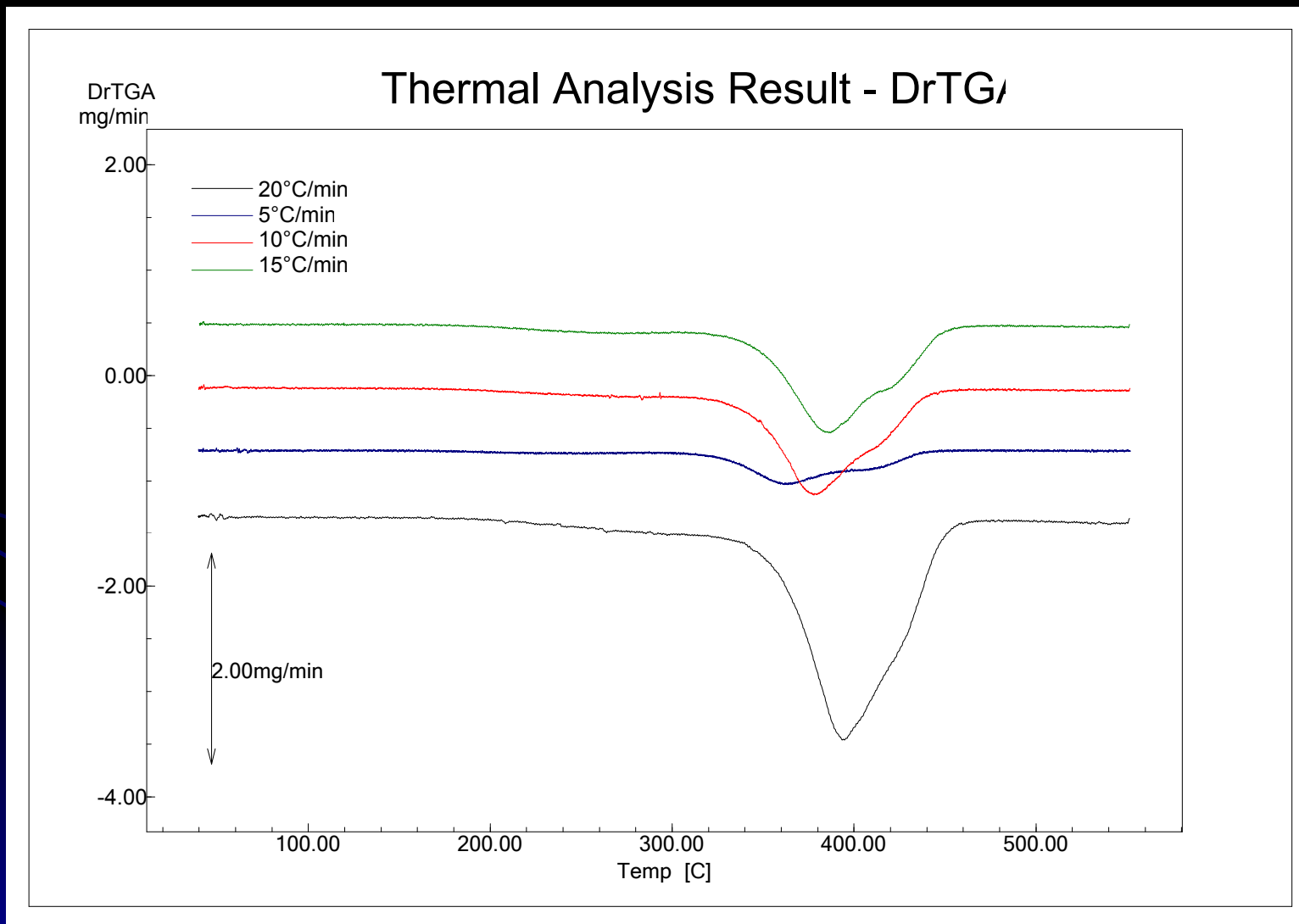


Thermal analysis of rubber

1. Step, volatile components, which are driven off between room temperature and approx. 320°C. They chiefly comprise added oils and other plasticizers, as well as moisture, solvent residues, monomers and, e.g. stearic acid.
2. Step, content of elastomers, such as natural rubber and EPDM. Under nitrogen atmosphere and the usual heating rate of 10°C/min, pyrolysis follows between 320 and 550°C, depending on the chemical structure of the elastomer molecule.
3. Residue: Inorganic fillers and carbon black.



Derivative TGA



Differential thermal analysis

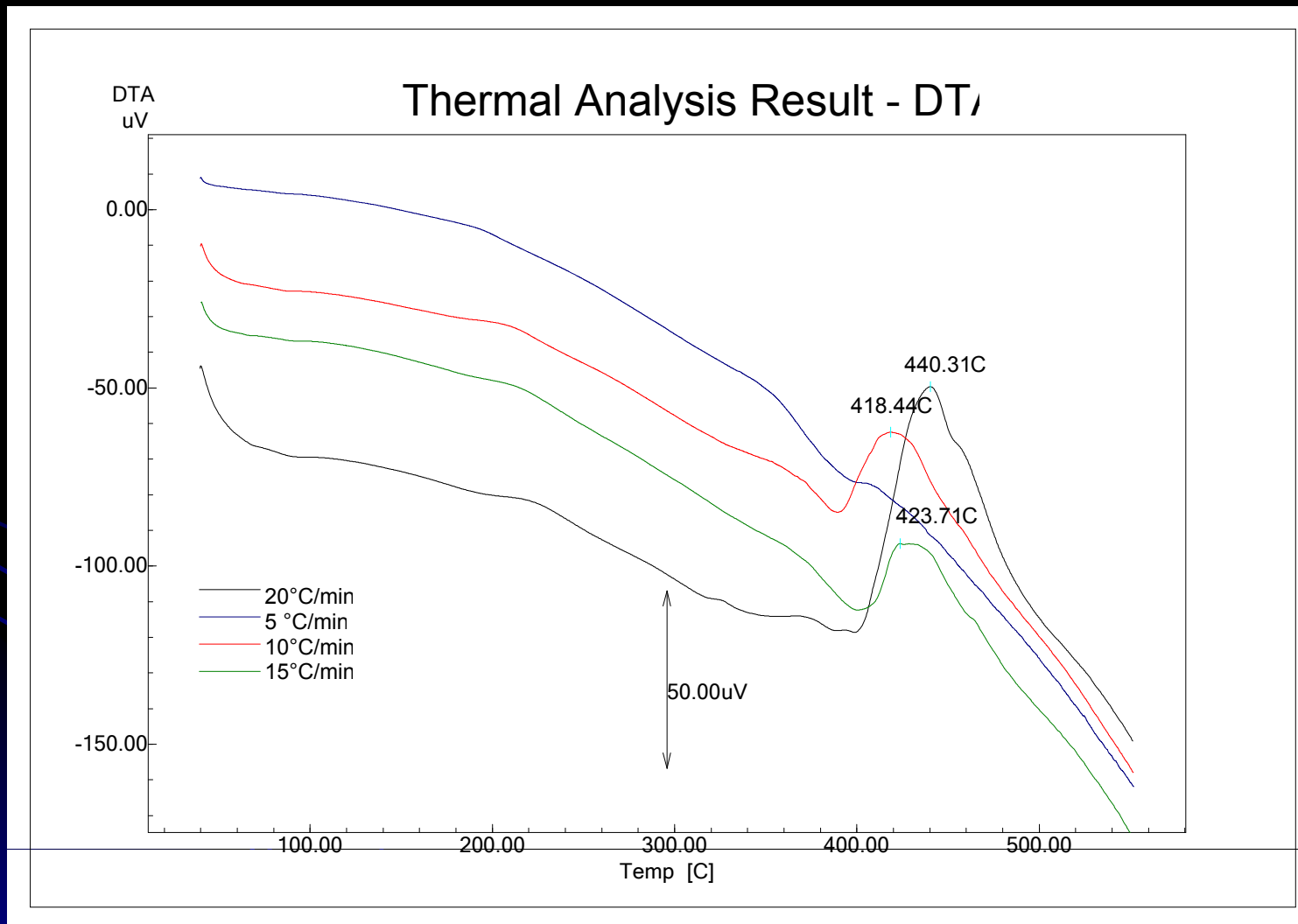


Table: TGA analysis at heating rate 10°C/min.

Step	Weight loss (%)
Volatile	8 %
Pyrolysis	57%
Residue	34 %

Table: DrTGA and TGA analysis hyper elastic rubber.

Heating rate (°C/min)	Peak DrTGA (°C)	Peak DTA (°C)
5	361.4	-
10	377.9	418.4
15	386.0	423.7
20	393.5	440.3



Model of Kinetics

The methods take their origin in the single-step kinetic equation:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha)$$

Ozawa, Flynn, Wall

$$\log \beta_i = \text{Const.} - \frac{0,4567 E_a}{RT_{\alpha,i}}$$

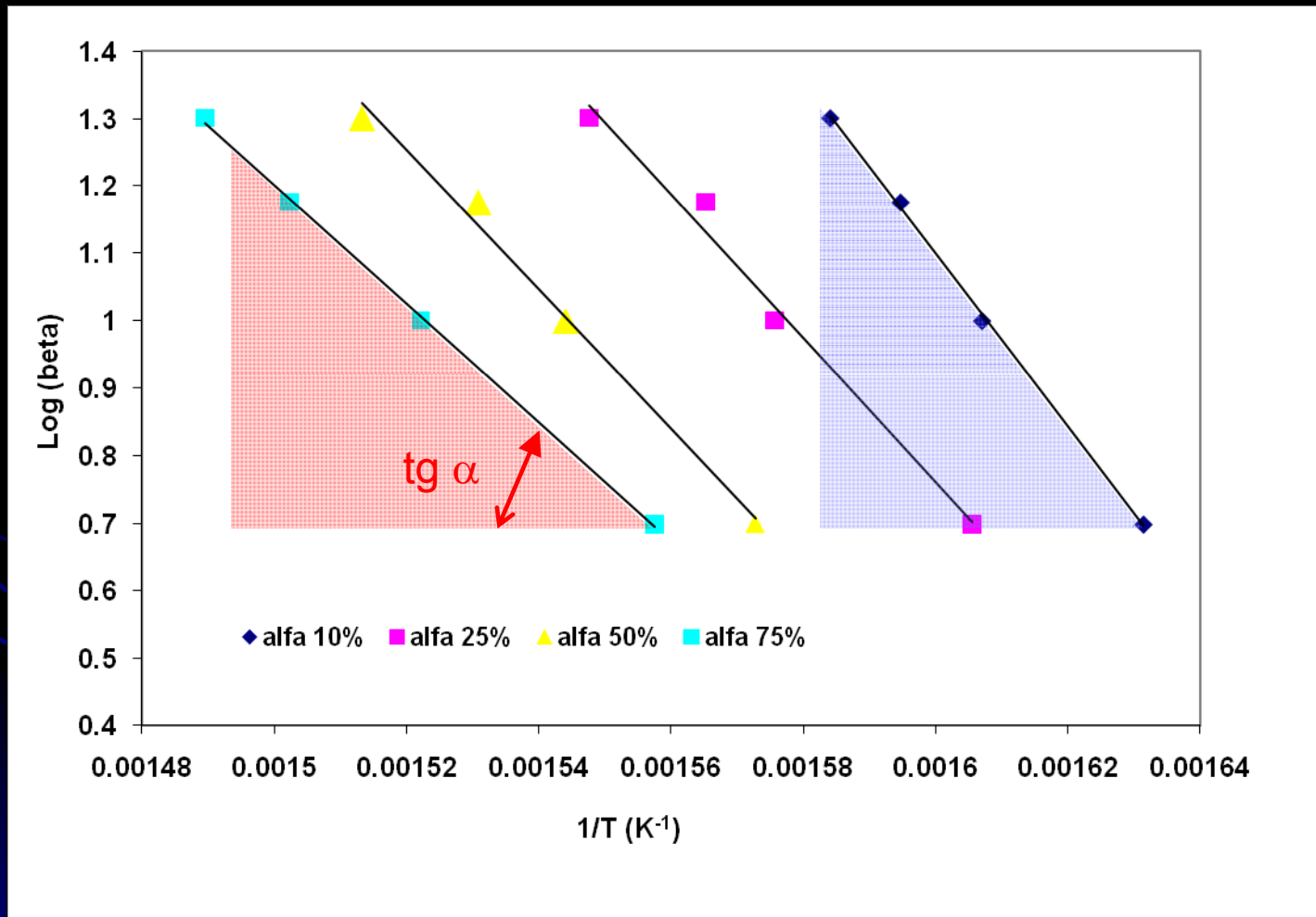
Kissinger

$$\ln\left(\frac{\beta}{T_M^2}\right) = \text{Const.} - \frac{E_a}{RT_M}$$

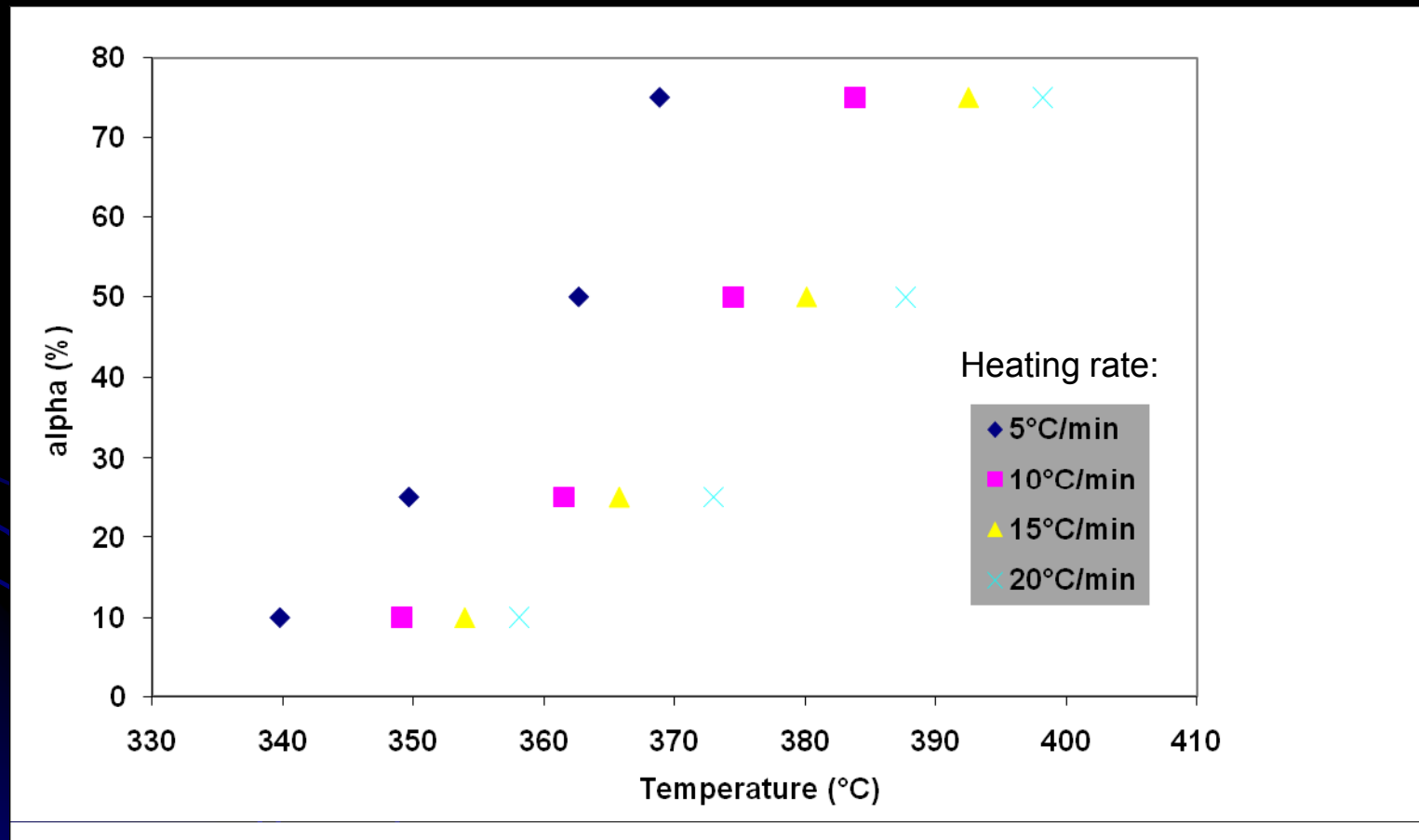
This formula is recommended by the American Society for Testing and Materials (ASTM) (E698-79, Appendix X3, Philadelphia, PA, 1979).



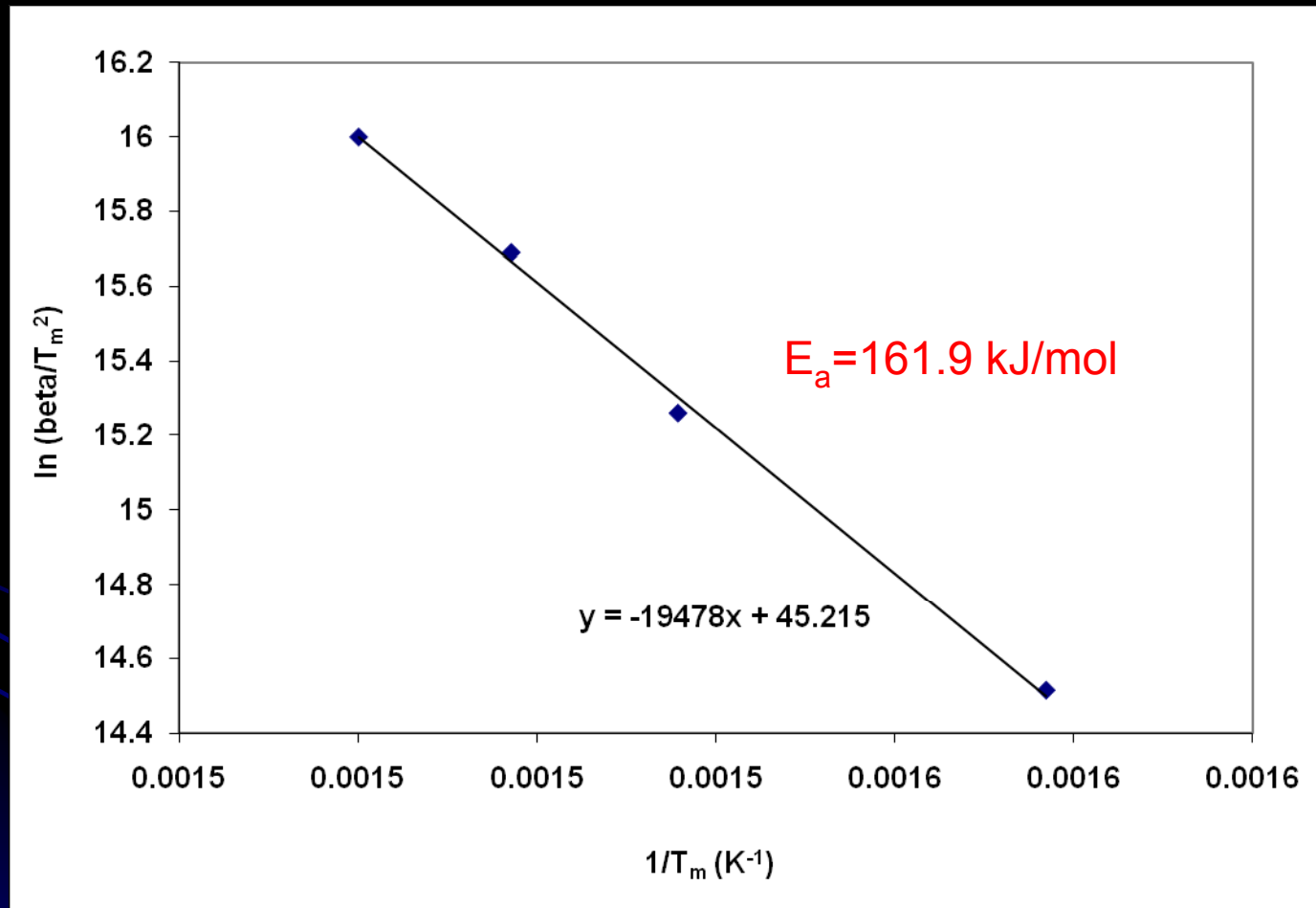
Kinetics by OFW



The conversion curve

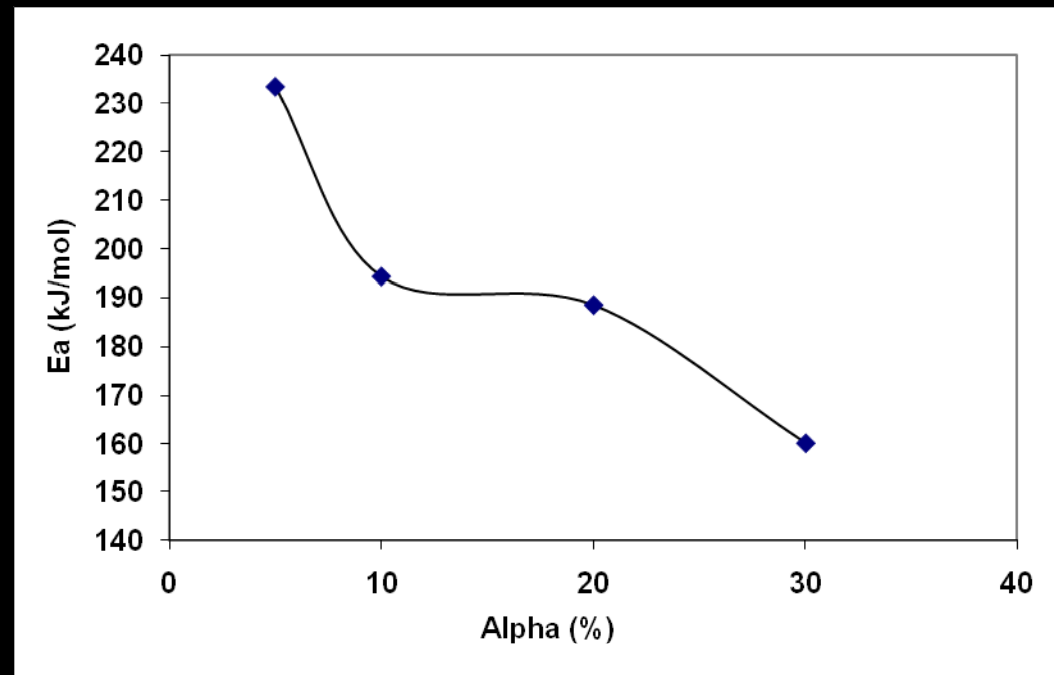


Kinetics by Kissinger



Kinetics

Alpha (%)	E_a (kJ/mol)
10	233.5
25	194.4
50	188.6
75	160.3
Kissinger	161.9



Conclusions

- Aim of this study was to enable determination of material constants needed for FEM calculation on real part modeling of mechanical properties as well as for feedback for material composition optimization.
- Based on thermal analysis, the thermal stability of the tested material was characterized, rates of degradation and starting decomposition temperatures were determined. It was found, that the activation energy was changed during degradation process reflecting consecutive manifold competing steps of polymer degradation.

Acknowledgements

Authors would like to express their gratitude for financing of this research by Ministry of Education, Youth and Sports of the Czech Republic (Grant VZ MSM7088352101) and to TRW Automotive Higher Education Grant (DV290001149-2601-UN).

Thank you for your attention.

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