THE APPLICATION OF ISO-CONVERSIONAL MODELS ON THE CURING KINETICS OF UREA-FORMALDEHYDE ADHESIVE IN THE PRESENCE OF WOOD

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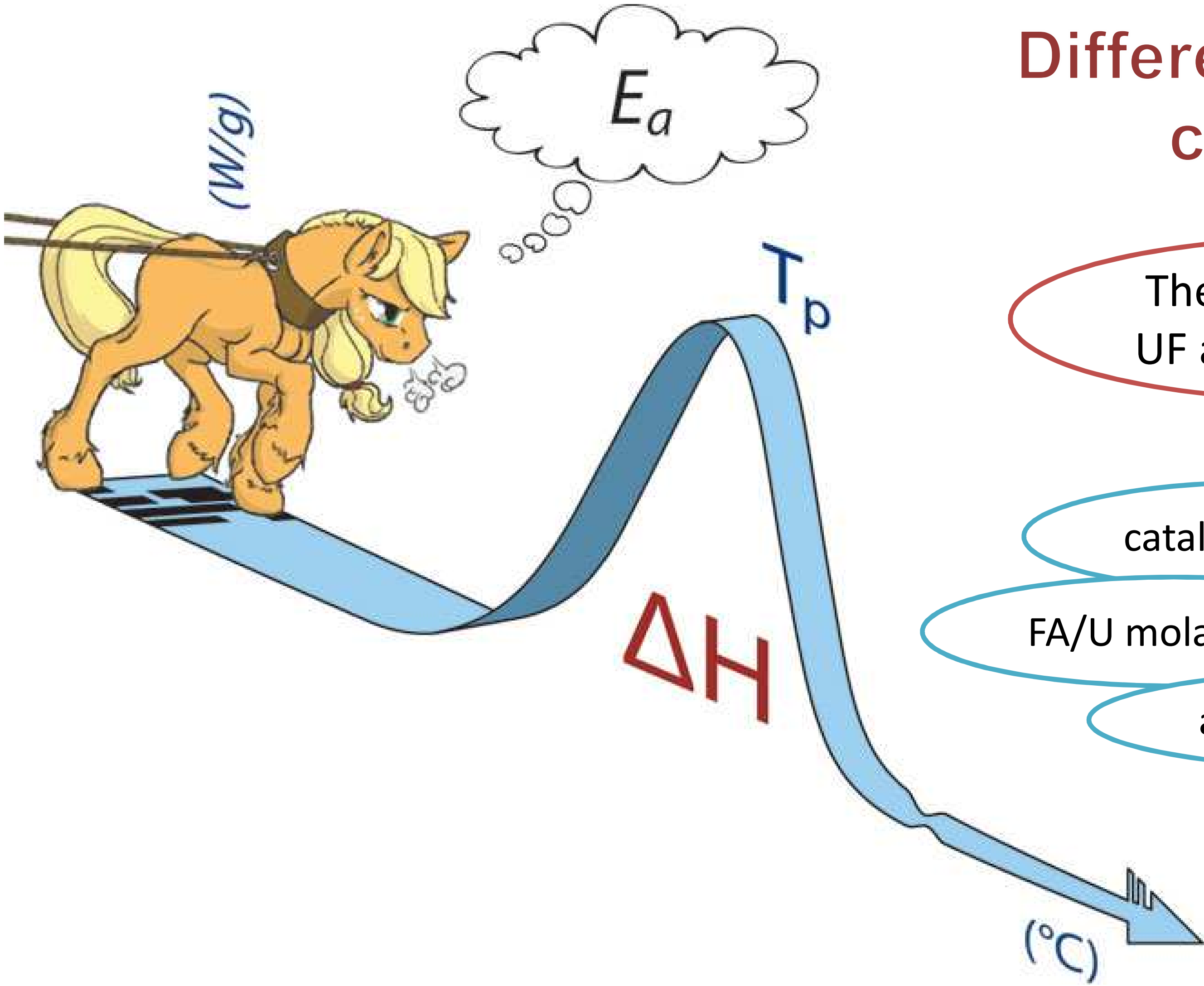


Differential scanning calorimetry

The applications on UF adhesive systems

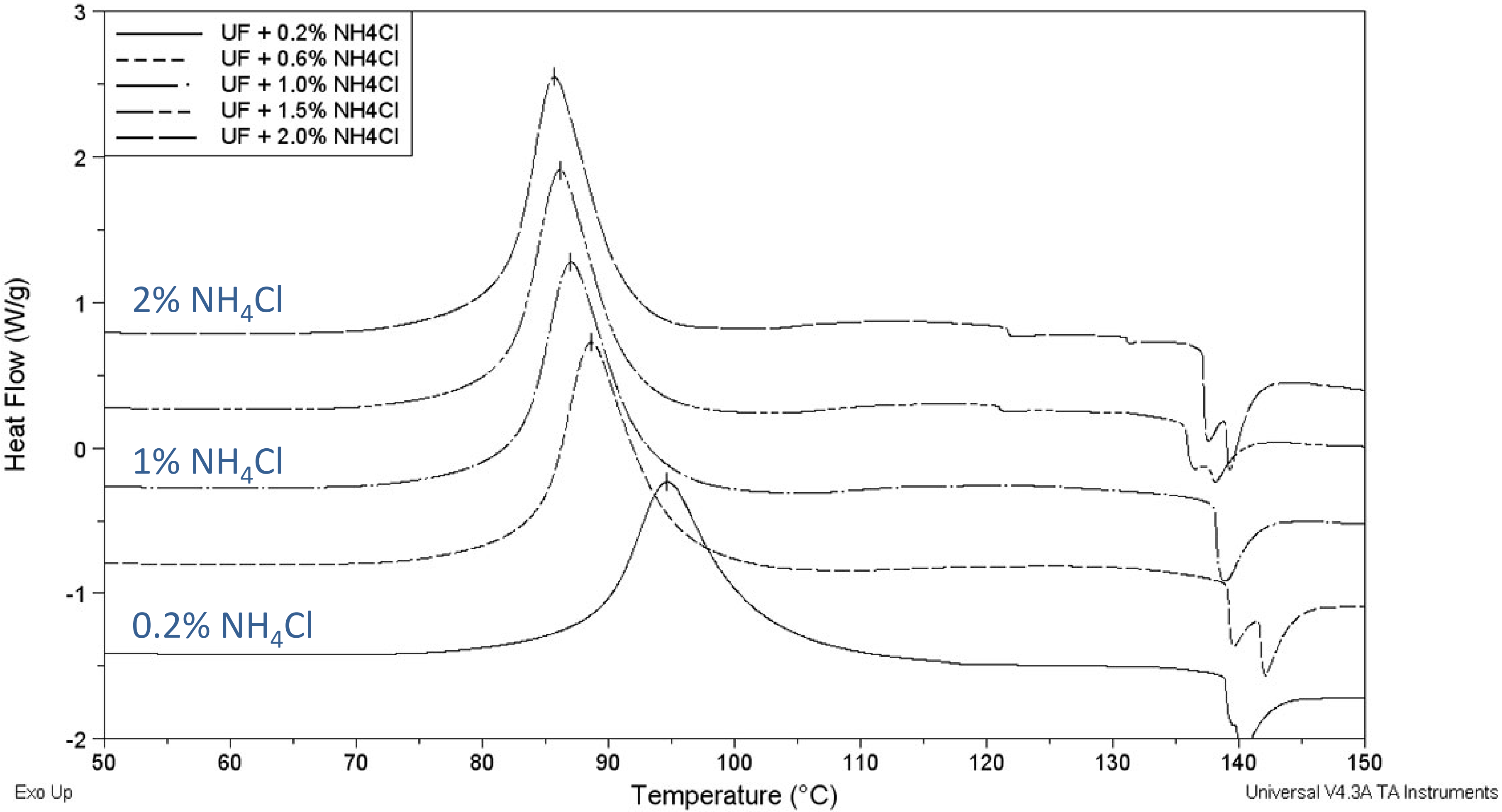
catalyst addition

FA/U molar ratio

adhesive modifications

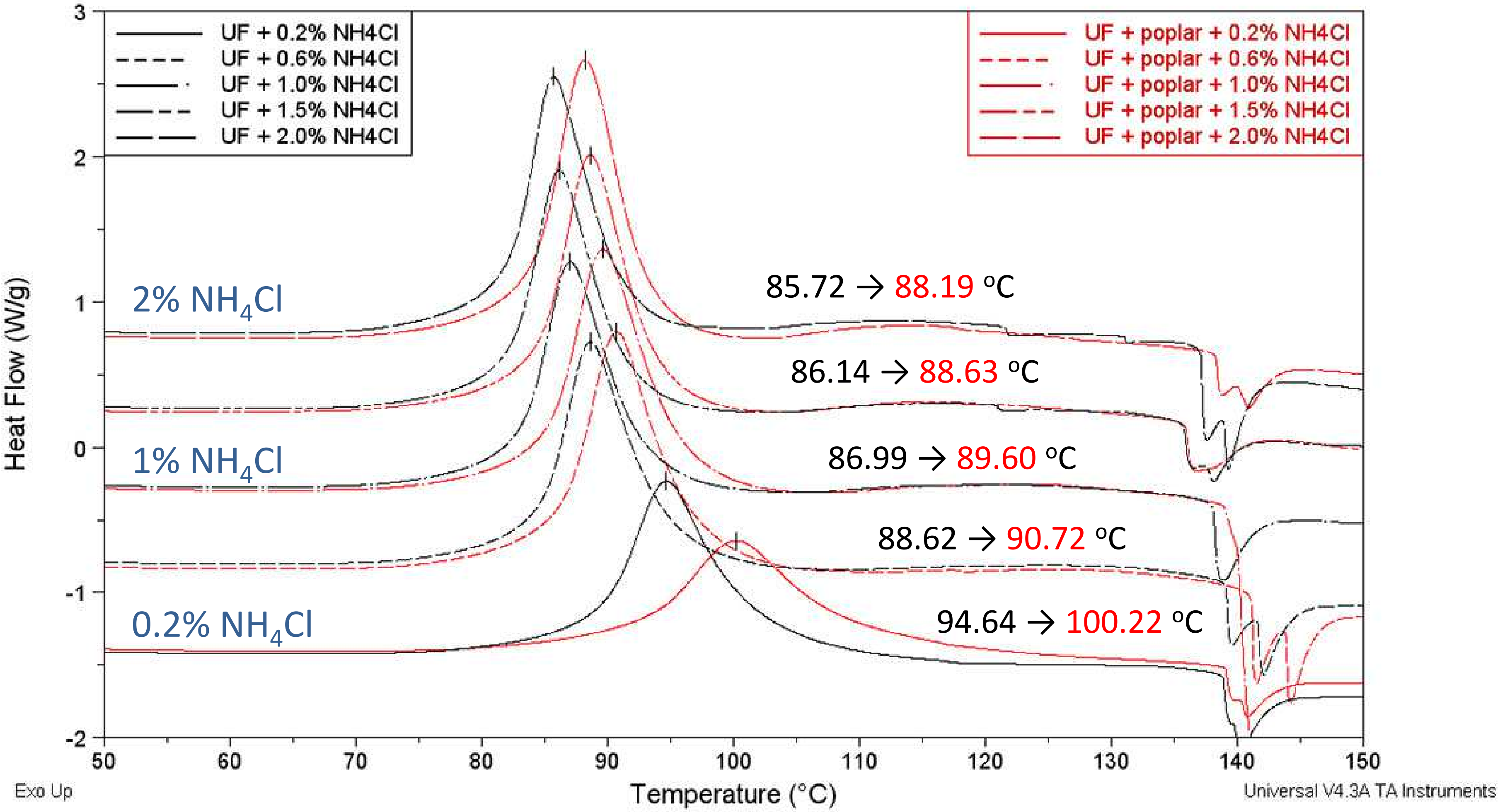
- Background
  - Effects of **wood species** on the UF adhesive cure:
    - Curing kinetics of UF adhesive - DTA and DSC studies have showed the influence of wood species (*Mizumachi 1973, Xing et al. 2004, Gao et al. 2007, Popovic et al. 2011*).

Influence of the catalyst addition --- at the constant heating rate: β = 10 °C/min



Influence of the catalyst addition --- at the constant heating rate: β = 10 °C/min

+ the addition of 10% of poplar wood flour



MATERIALS

- UF adhesive:
  - Commercial UF adhesive obtained from Nafta Petrohem (Lendava, Slovenia) with F/U molar ratio of 1.12.
  - Hardener: ammonium chloride (NH_4Cl)
- Wood flour:
  - **fir** (*Abies alba / Mill*),
  - **beech** (*Fagus moesiaca / Domin, Maly/Czeczott.*),
  - **poplar** (*Populus x Euroamericana 'I-214'*).
  - The fraction of wood flour screened through 0,15 mm mesh.
  - The addition of wood flour to UF adhesive = 10% per od. wt.

METHODS

- DSC measurements:
  - DSC Q20 (TA Instruments, USA),
  - Dynamical scanning regime,
    - Heating rates (β): 5, 10, 15 i 20 ^{o}C/min
    - Temperature range: 40 - 200 ^{o}C
  - Purge gas: nitrogen
  - Aluminum pans (hermetically sealed)
  - The amount of UF adhesive samples: approx. 4 to 5 mg
  - The instrument software: TA Universal Analysis

METHODS

➡ Samples:

(UF adhesive diluted to 50% of dry matter)

- UF adhesive + 0,2% NH_4Cl (control)
- UF adhesive + 0,2% NH_4Cl + 10% beech wood flour,
- UF adhesive + 0,2% NH_4Cl + 10% fir wood flour,
- UF adhesive + 0,2% NH_4Cl + 10% poplar wood flour.

METHODS

➡ Isoconversion kinetic models

- Peak temperature (*Tp*) occurs at the maximum value of *dα/dt*;
- Reaction rate is a function of temperature, at a given degree of conversion (*α(T)*).

β - heating rate, in °K/s;
E_a - activation energy, in J/mol;
R - ideal gas constant, 8.314 J/(mol·K);
T - reaction temperature, in °K;
α - reaction degree.

Ozawa-Flynn-Wall

$$\log(\beta) = A' - 0.4567 \cdot \frac{E}{R \cdot T} \qquad A' = \left[\frac{k_0 \cdot E_a}{R \cdot g(\alpha)}\right] - 2.315$$

logβ vs. 1/T

Kissinger-Akahira-Sunose

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{R \cdot A}{E_a \cdot g(\alpha)}\right) - \frac{E}{R \cdot T}$$

ln(β/T²) vs. 1/T

Friedman

Requires reaction rate (dα/dt) at T(β)

$$\ln\left(\beta \frac{d\alpha}{dT}\right) = -\ln f(\alpha) - \frac{E}{R \cdot T}$$

ln(β·dα/dt) vs. 1/T

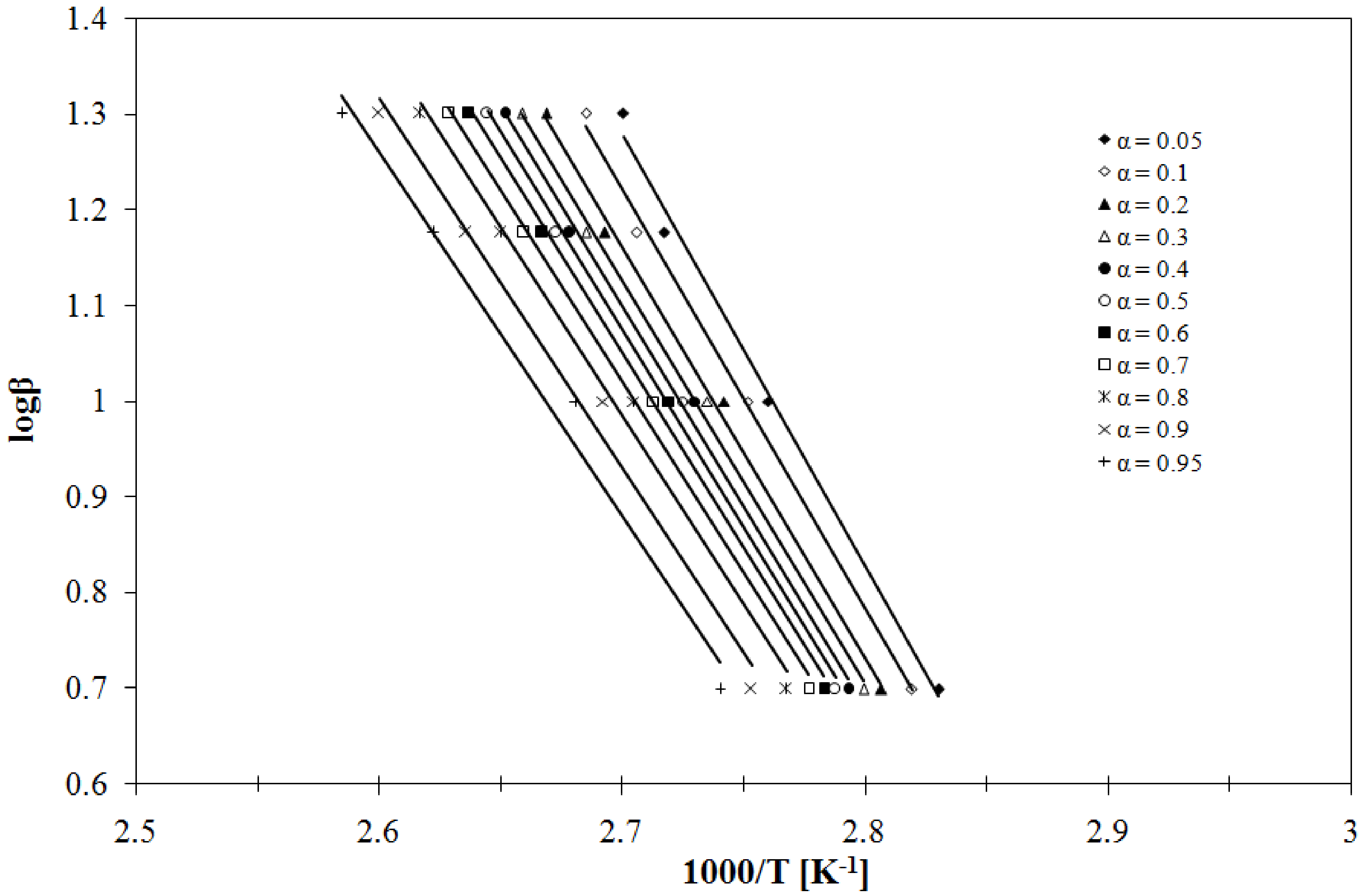
RESULTS & ANALYSIS

➡ *The application of <u>simple</u> Kissinger method --- single values of E_a !!!*

Peak temperatures — Energy of activation

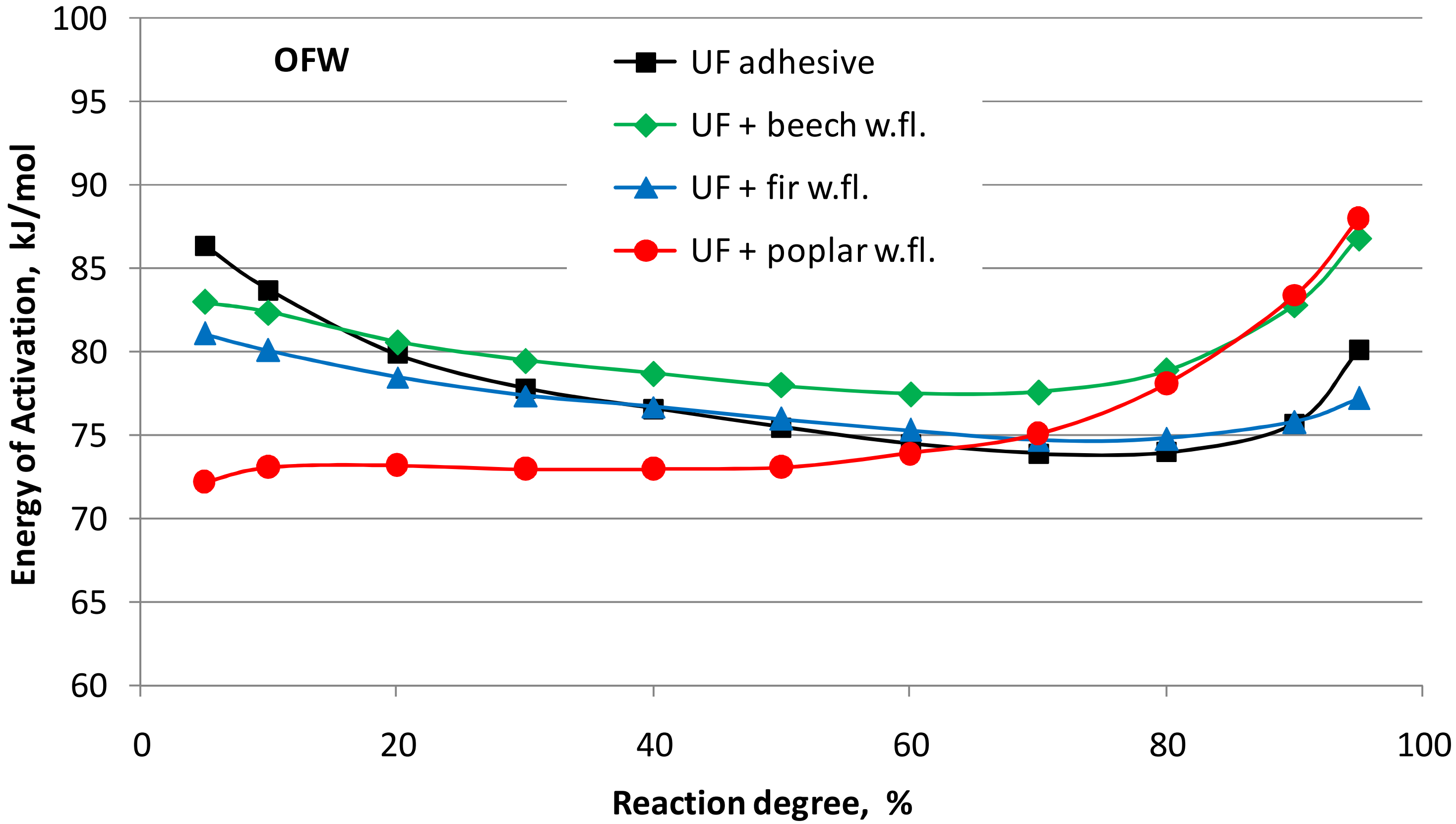
	T_p (°C)				Function	E_a (kJ/mol)
β (°C/min)	5	10	15	20	← Heating rate	
UF adhesive	85,6	95,0	101,3	105,0	$y = 8.856x - 14.53$ $R^2 = 0.9991$	**73.6**
UF + beech	87,8	97,8	102,7	106,8	$y = 9.29x - 15.55$ $R^2 = 0.9979$	**77.2**
UF + fir	87,5	97,2	103,6	107,0	$y = 8.84x - 14.33$ $R^2 = 0.9981$	**73.5**
UF + poplar	89,8	100,2	106,2	110,6	$y = 8.527x - 13.31$ $R^2 = 0.9996$	**70.9**

RESULTS & ANALYSIS



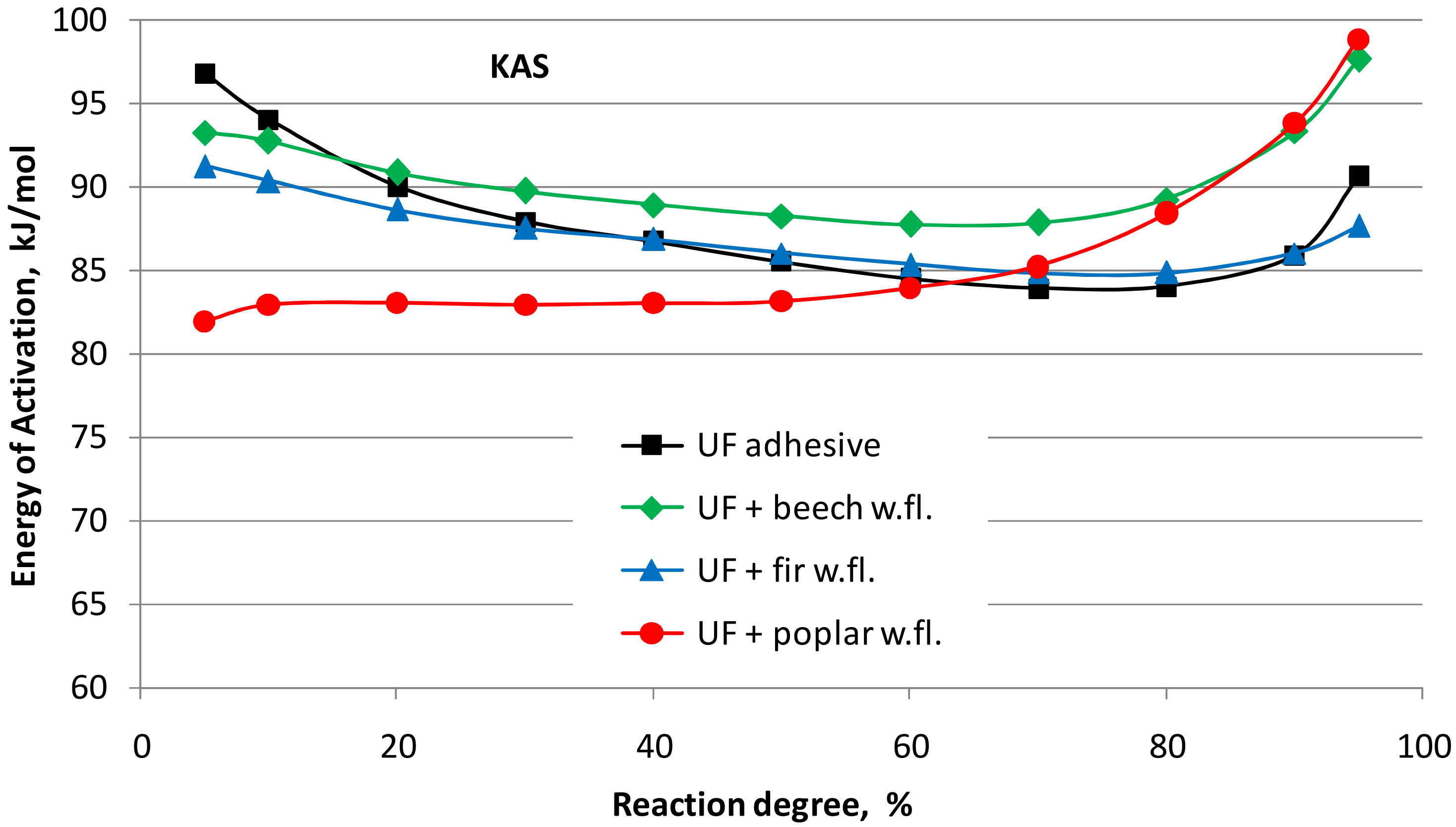
Isoconversion functions for different degrees of curing reaction of UF adhesive control sample (OFW method)

RESULTS & ANALYSIS



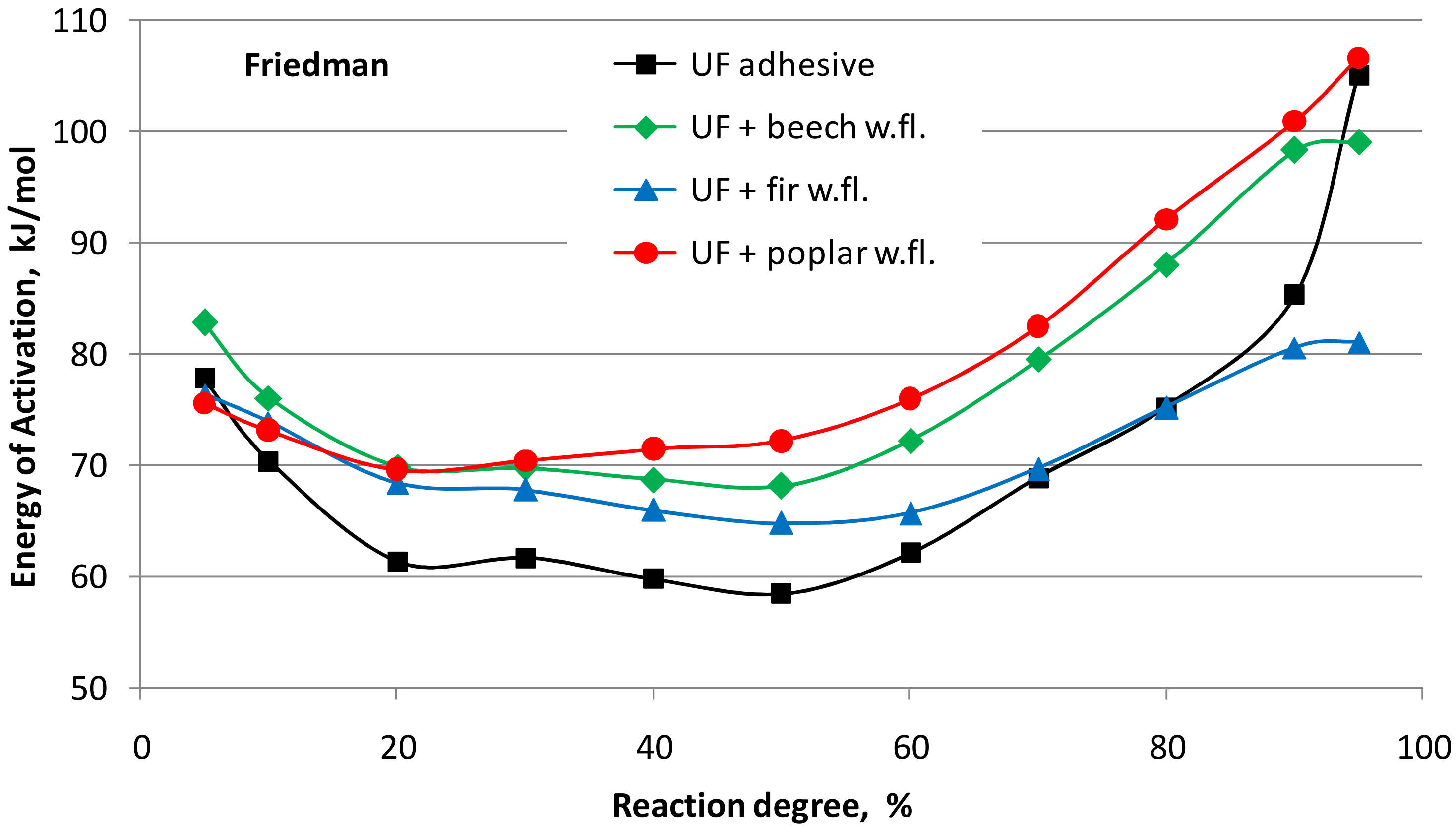
E_a dependence on the reaction degree (α) for the ***Ozawa-Flynn-Wall*** *isoconversion model*

RESULTS & ANALYSIS



E_a dependence on the reaction degree (α) for the ***Kissinger-Akahira-Sunose*** *isoconversion model*

RESULTS & ANALYSIS



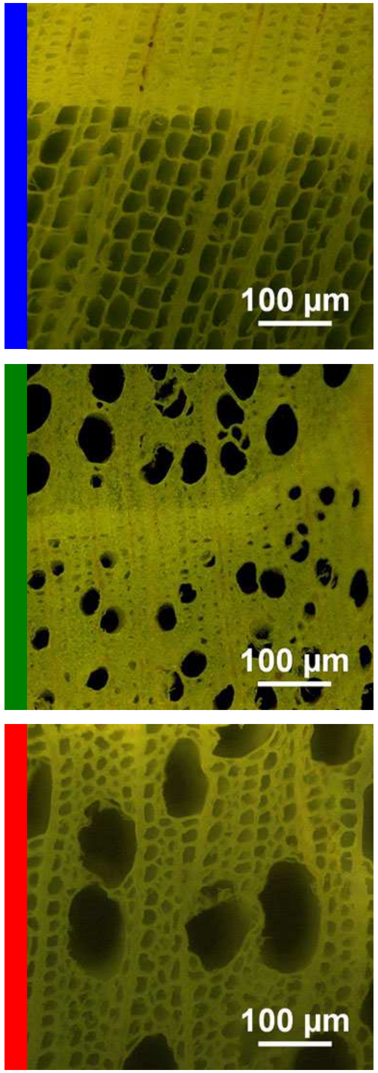
*E_a dependence on the reaction degree (α) for the **Friedman** isoconversion model*

CONSIDERATIONS

- The effects of wood species on the UF adhesive cure:
  - Anatomical aspects
  - Chemical aspects

CONSIDERATIONS

Wood species



Fir

Tracheid system;
high porosity

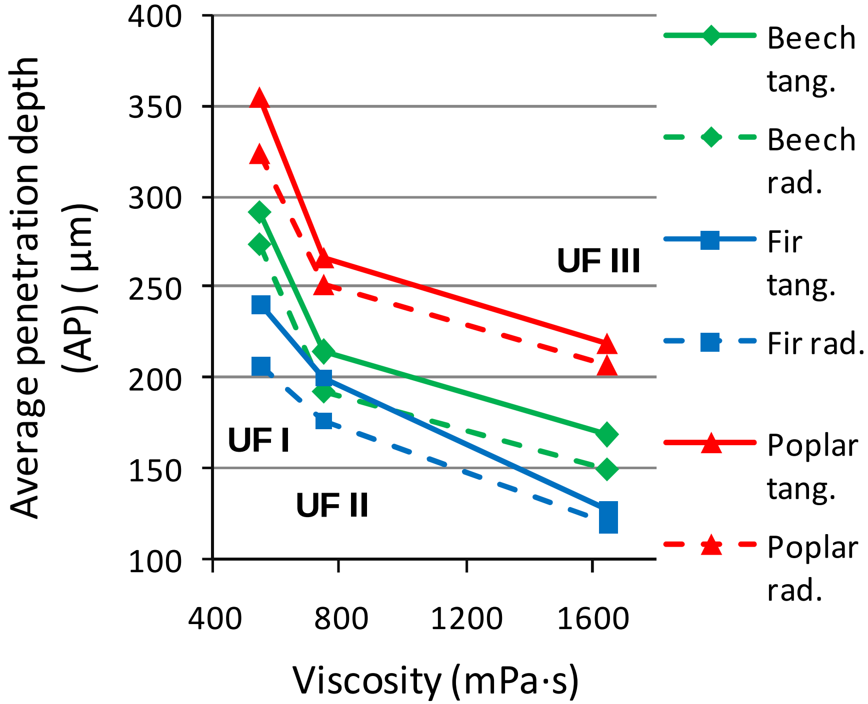
Beech

Vessels as main transport elements;
low porosity

Poplar

Vessels as main transport elements;
high porosity

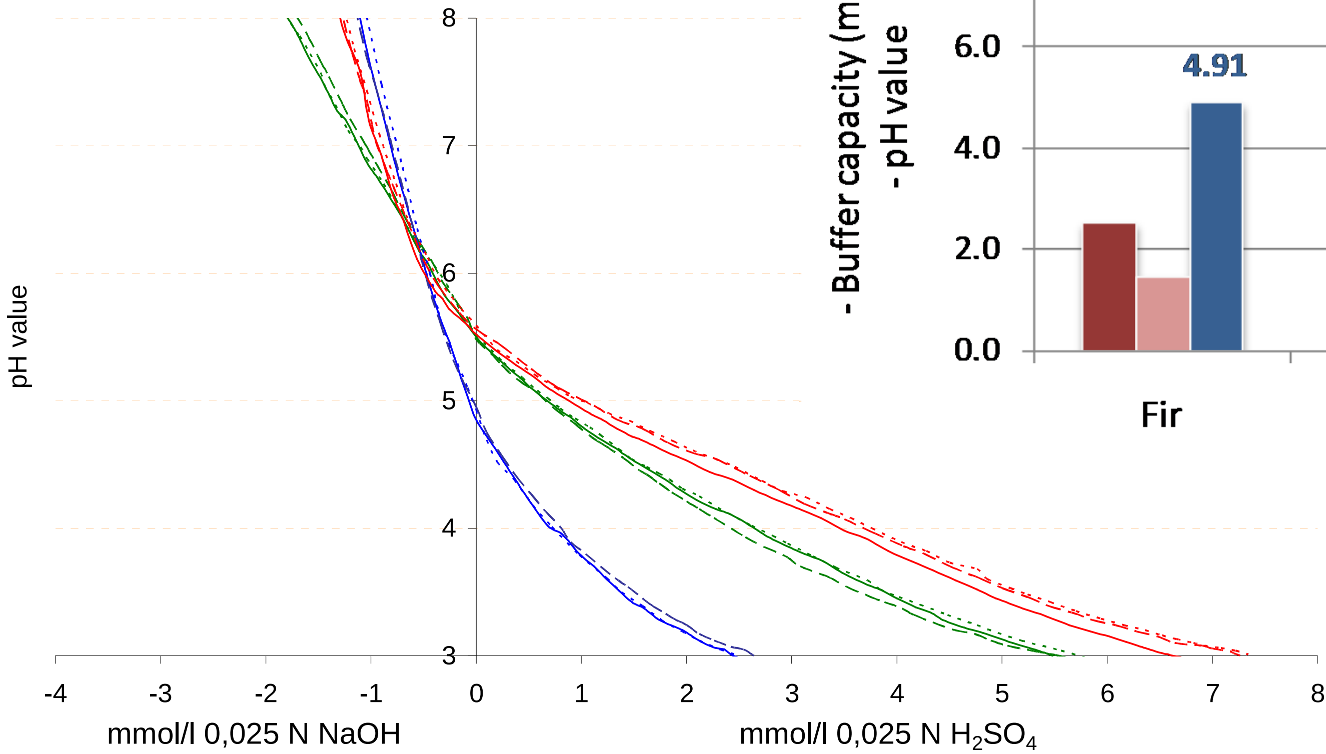
Anatomical aspects

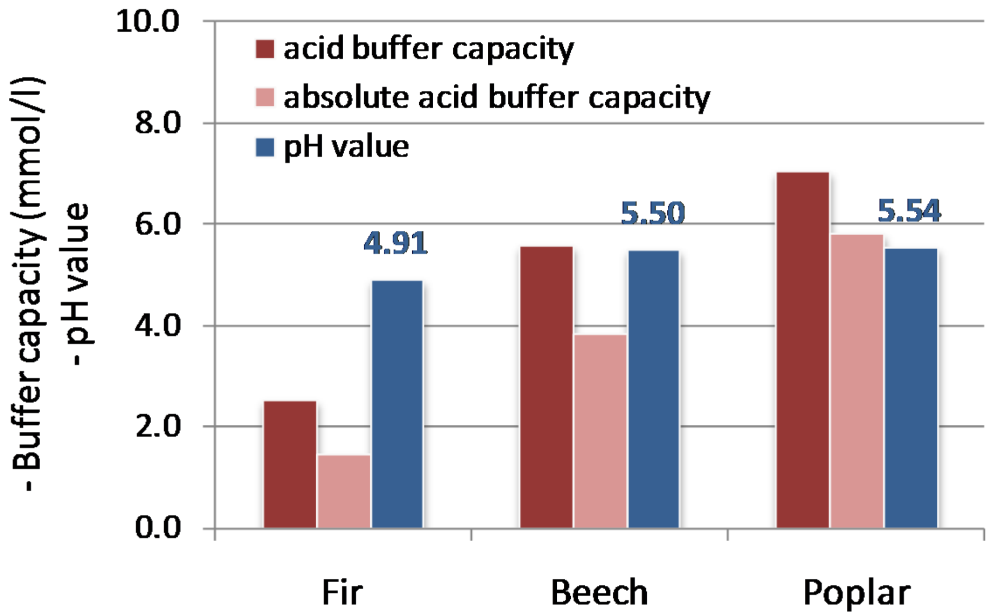


[Gavrilovic et al. 2013]

CONSIDERATIONS

Chemical aspects





[Popovic et al. 2013]

CONCLUSIONS

- Similar patterns between the Ozawa-Flynn-Wall and the Kissinger-Akahira-Sunose isoconversional models.
- KAS model showed higher values than OFW.
- Both OFW and KAS models do not coincide completely with the peak temperatures of the curing reaction.
- The curing reactions of the UF adhesive systems with wood flour are presented more accurately with the Friedman model (coincides well with the peak temperature values).

THANK YOU...