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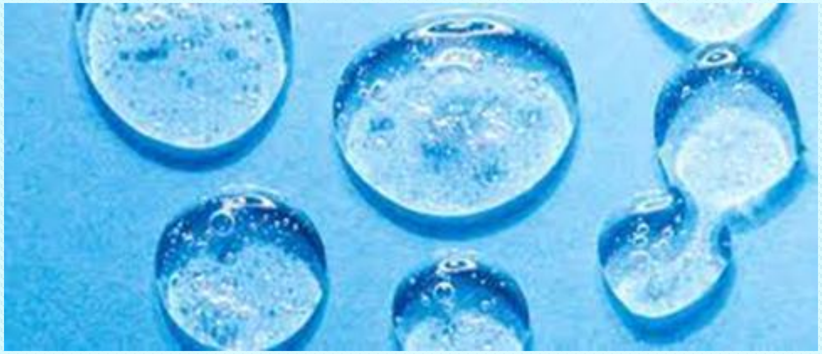
Linear and non-linear methods applied to fitting non-isothermal kinetic curves of dehydration of PAAG hydrogel swollen to equilibrium and non-equilibrium state



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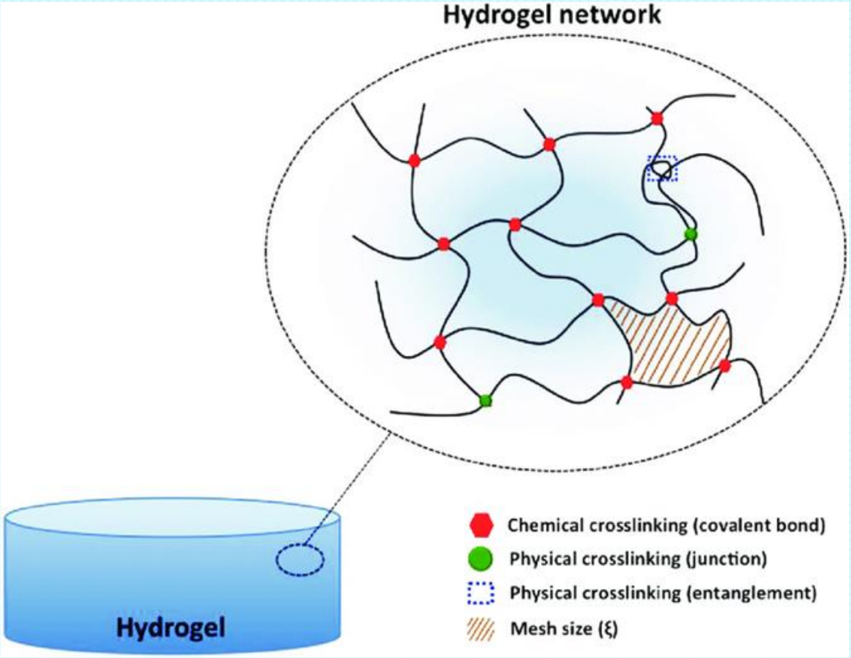
Hydrogels

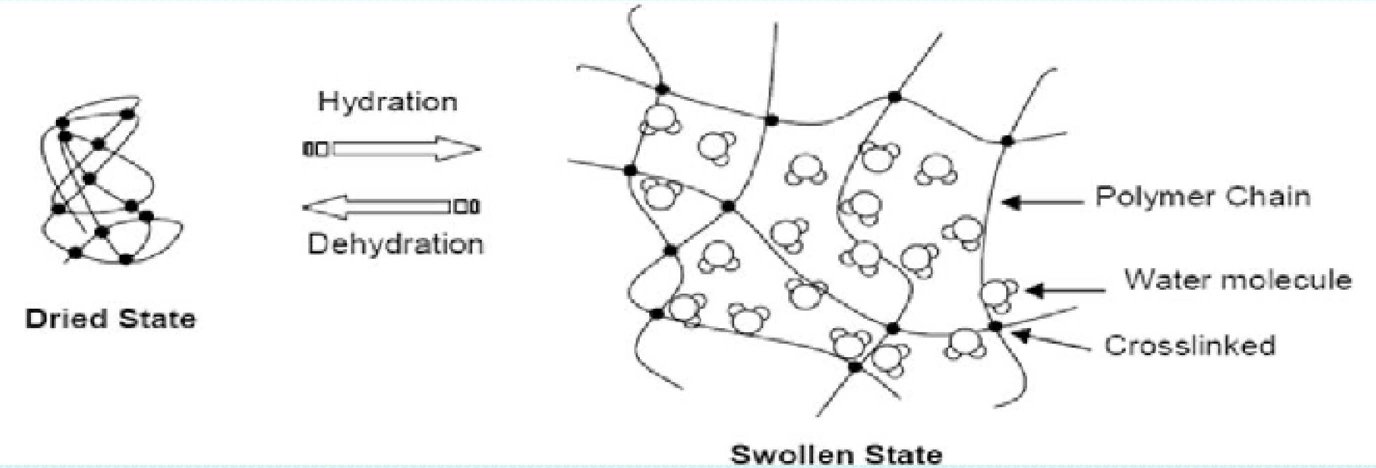
- Three-dimensional cross-linked polymeric structures.
- They are able to absorb significant amounts of water, water solutions and biological liquids, without dissolowing or losing their structural integrity.



Hydrogels can be used:

- Agriculture
- Drug delivery systems
- Hygenic products
- Tissiue engineering
- Biosensors
- Systems for aqueous pollutants removal

- The widest practical applications of the hydrogels are based on their ability to reversibily abosrb (swelling) and release (dehydrate) water.



Poly(acrylic acid)-g-gelatin (PAAG) hydrogel

Synthesis:

1. 0.5g of gelatin was dissoloved in 35ml distilled water at 318K under stirring, until clear, homogenous solution is obtained.
2. Water solution of the initiator VA-044 was added to gelatin solution and left for 15 min under stirring.
3. Acrylic acid (AA) was neutralized to pH=7 by adding KOH (aq.) under cooling (278K) with constat stirring.
4. Cross-linker solution was added to the gelatin-initiator solution.
5. The mixture of neutralized AA and cross-linker was added to the gelatin-initiator solution.
6. The reaction mixture was once again rapidly stirred, immediately poured into Teflon mold, and placed in an oven at 353 K, for 3h.

7. The resulting gel-type products were cut into disks, and washed out with distilled water to remove the sol fraction. The water was changed every 2-3 h for 7 days.
8. After that, the washed-out hydrogels were air dried in an oven at 353 K until constant mass was attained.
9. The obtained products PAAG xerogels were stored in a vacuum exicator until use.
10. For this investigation the obtained PAAG xerogels were allowed to swell to varyng swelling degree in distilled water at room temperature.

Thermogravimetric measurements

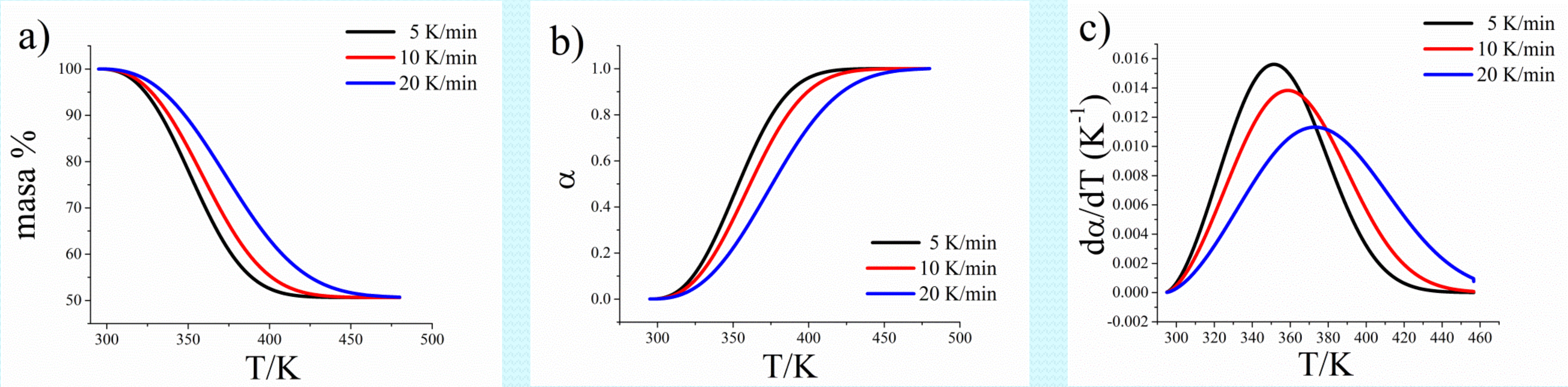


Figure1. Obtained curves for non-isothrermal dehydratition of (1:1) PAAG hydrogel at different heating rates: a) the thermogravimetric curves, b) the conversion curves and c) the differential conversion curves

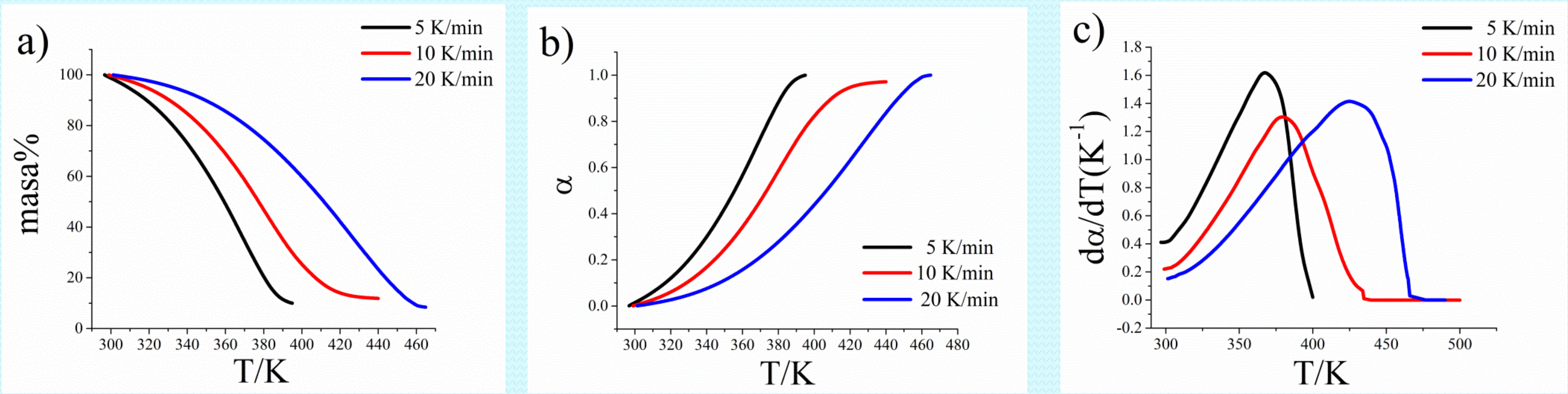


Figure 2. Obtained curves for non-isothrermal dehydratition of (1:10) PAAG hydrogel at different heating rates: a) the thermogravimetric curves, b) the conversion curves and c) the differential conversion curves

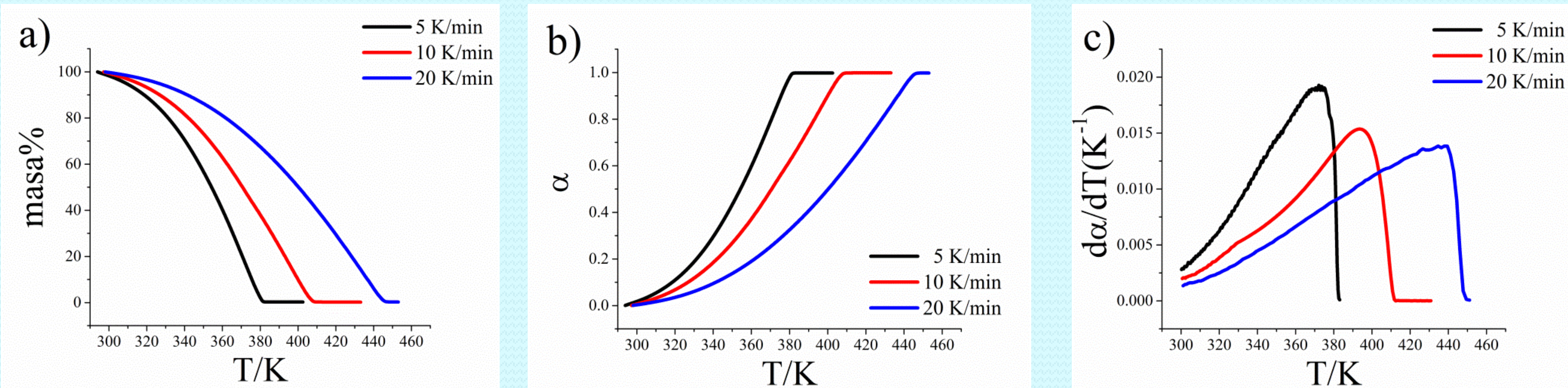


Figure 3. Obtained curves for non-isothrermal dehydratition of equilibrium swollen PAAG hydrogel at different heating rates: a) the thermogravimetric curves, b) the conversion curves and c) the differential conversion curves

The mechanisms and kinetics of the dehydration PAAG hydrogel

- The mechanism and kinetics of dehydration of hydrogels is not known enouh or is not well explained.

- The main goal of this work was to describe the kinetics of non-isothermal dehydration of poly(acrilic acid)-g-gelatin (PAAG) hydrogel that was swollen in distilled water to different swelling degrees.

The Weibull distribution function of reaction times:

$$\alpha = 1 - \exp\left(-\left(\frac{T - T_0}{v_{\mathrm{h}}\,\eta}\right)^{\beta}\right)$$

Where is:

α – degree of dehydration

T, T_0 - current and initial temperatures of the non-isothermal dehydration respectively

v_{h} - heating rate

β, η – the Weibull distribution parameters

Calculation of the Weibull parameteres by linear fitting of conversion curves

- Linear form of the Weibull distribution fuction:

$$\ln[-\ln(1-\alpha)] = \beta \ln\left(\frac{1}{\eta}\right) + \beta \ln\left(\frac{T-T_0}{v_h}\right)$$

$$\ln[-\ln(1-\alpha)] = f\left(\ln\left(\frac{T-T_o}{v_h}\right)\right)$$

- The Weibull parameters β and η are calulated from slope and intercept respectively.

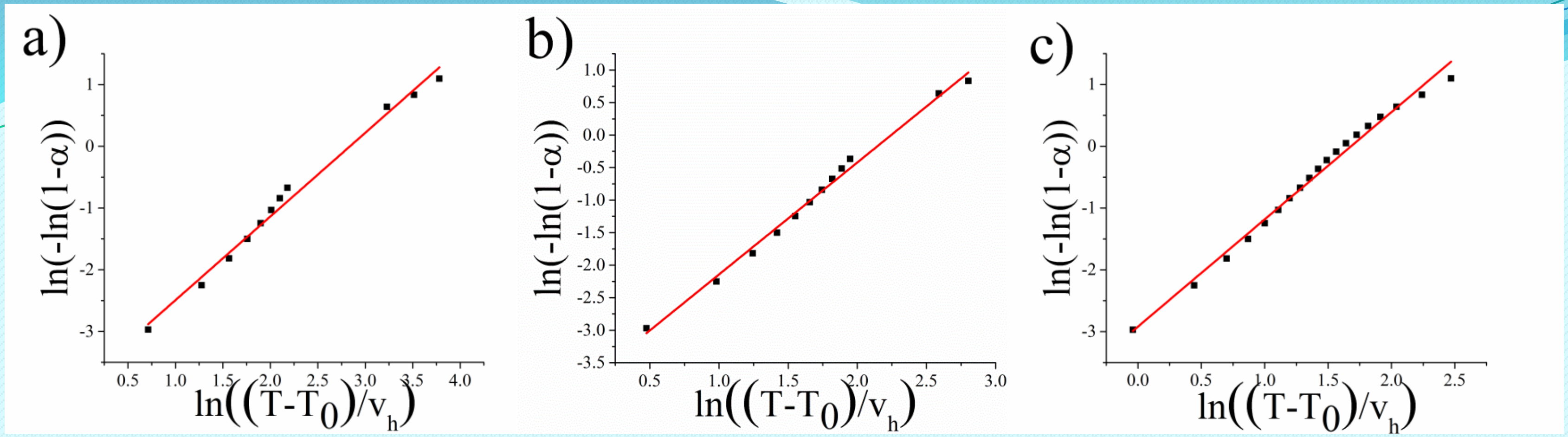


Figure 4. Determination of the Weibull parameters for (1:1) PAAG hydrogel at different heating rates: a) 5 K/min b) 10 K/min i c) 20 K/min

Table 1. The values of the Weibull parameters obtained by linearization of conversion curves for (1:1) PAAG hydrogel at different heating rates and the coefficient of determination R^2

Heating rate v_h (K/min)	β	η	R^2
5	$2{,}28 \pm 0{,}01$	$13{,}68 \pm 0{,}01$	0,989
10	$2{,}28 \pm 0{,}01$	$7{,}72 \pm 0{,}01$	0,993
20	$2{,}27 \pm 0{,}01$	$4{,}71 \pm 0{,}01$	0,989

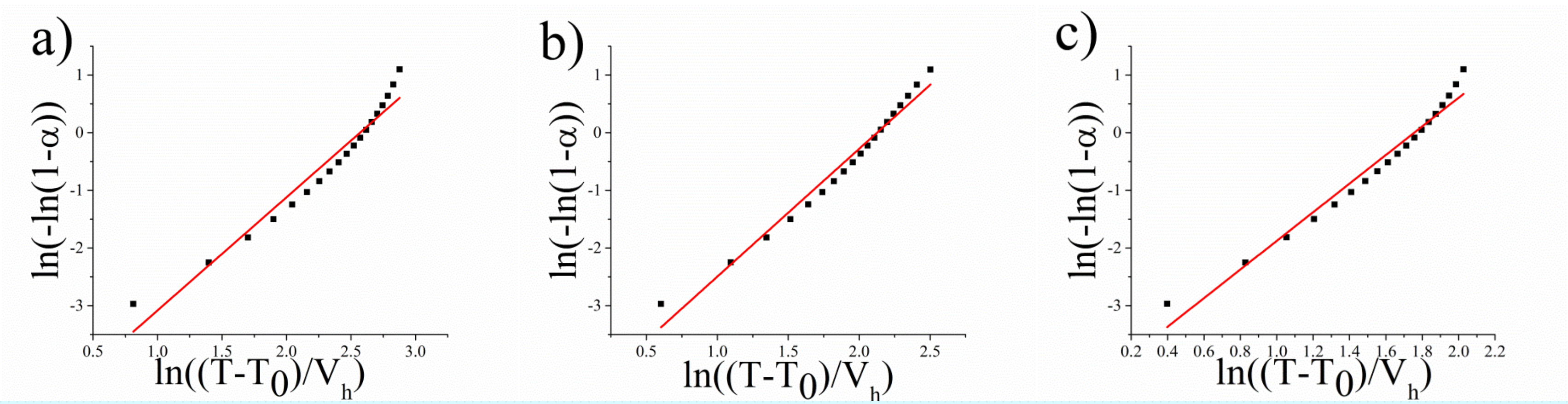


Figure 5. Determination of the Weibull parameters for (1:10) PAAG hydrogel at different heating rates: a) 5 K/min b) 10 K/min i c) 20 K/min

Table 2. The values of the Weibull parameters obtained by linearization of conversion curves for (1:10) PAAG hydrogel at different heating rates and the coefficient of determination R^2

Heating rate v_h (K/min)	β	η	R^2
5	2,68 ± 0,01	13,54 ± 0,01	0,951
10	2,79 ± 0,01	7,38 ± 0,01	0,975
20	2,92 ± 0,01	4,65 ± 0,01	0,967

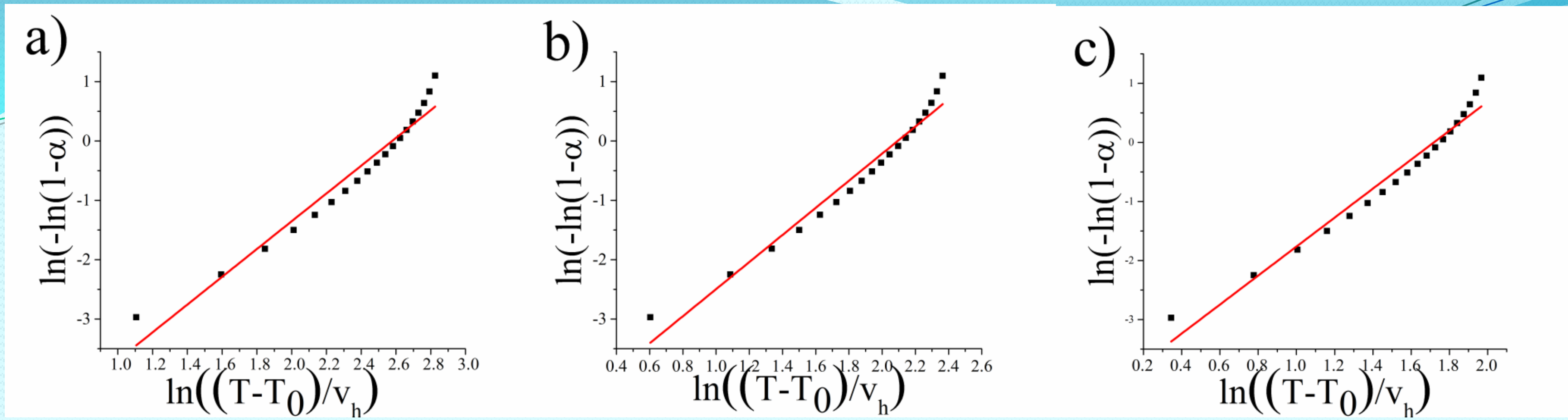


Figure 6. Determination of Wibull parameters for equilibrium swallen PAAG hydrogel at different heating rates: a) 5 K/min b) 10 K/min i c) 20 K/min

Table 3. The values Weibull parameters obtained by linearization of conversion curves for equilibrium swallen PAAG hydrogel at different heating rates and the coefficient of determination R^2

Heating rate v_h (K/min)	β	η	R^2
5	$2{,}91 \pm 0{,}01$	$13{,}15 \pm 0{,}01$	0,951
10	$2{,}87 \pm 0{,}02$	$7{,}04 \pm 0{,}01$	0,961
20	$2{,}93 \pm 0{,}02$	$4{,}37 \pm 0{,}01$	0,962

Obtaining the Weibull parameteres by non-linear fitting of conversion curves

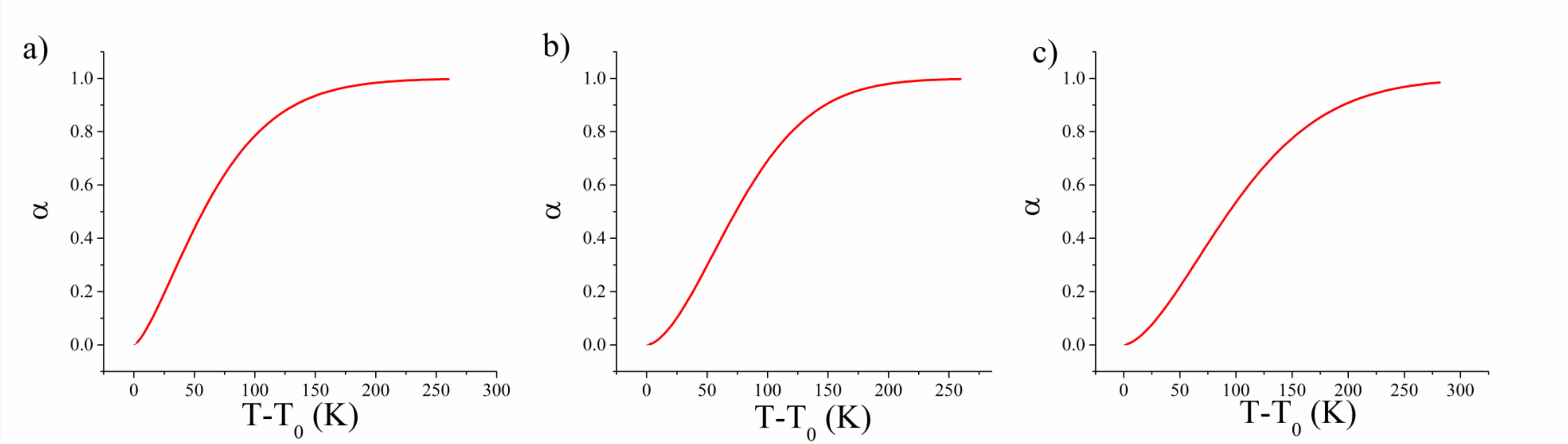


Figure 7. Nonlinear fitting of the Weibull function for (1:1) PAAG hydrogel at different heating rate: a) 5K/min, b) 10K/min and c) 20K/min

Table 4. Comparison of the Weibull parameters at different heating rates, obtained by linear and non-linear fitting for (1:1) PAAG hydrogel

	Linear fitting		Non-linear fitting	
Heating rate $v_h (K/min)$	β	η	β	η
5	$2,28 \pm 0,01$	$13,68 \pm 0,01$	1,42	14,79
10	$2,28 \pm 0,01$	$7,72 \pm 0,01$	1,73	9,11
20	$2,27 \pm 0,01$	$4,71 \pm 0,01$	1,64	5,88

The value of the parameter β, when applying non-linear regression analysis, is lower than the corresponding value for linear regression analysis.

The value of the parameter η, is higher when applying non-linear regression analysis than the corresponding value for linear regression analysis.

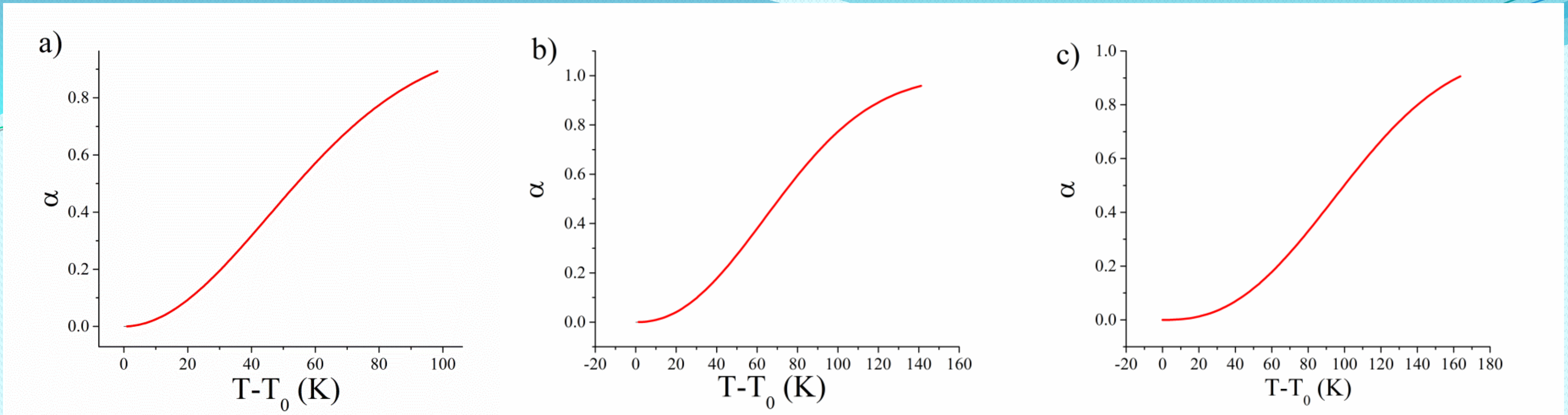


Figure 8. Nonlinear fitting of the Weibull function for (1:10) PAAG hydrogel at different heating rate: a) 5K/min, b) 10K/min and c) 20K/min

Table 5. Comparison of the Weibull parameters at different heating rates, obtained by linear and nonlinear fitting for (1:10) PAAG hydrogel

	Linear fitting		Non-linear fitting	
Heating rate $v_h(K/min)$	β	η	β	η
5	$2{,}68 \pm 0{,}01$	$13{,}54 \pm 0{,}01$	1,96	13,06
10	$2{,}79 \pm 0{,}01$	$7{,}38 \pm 0{,}01$	2,22	8,37
20	$2{,}92 \pm 0{,}01$	$4{,}65 \pm 0{,}01$	2,48	5,79

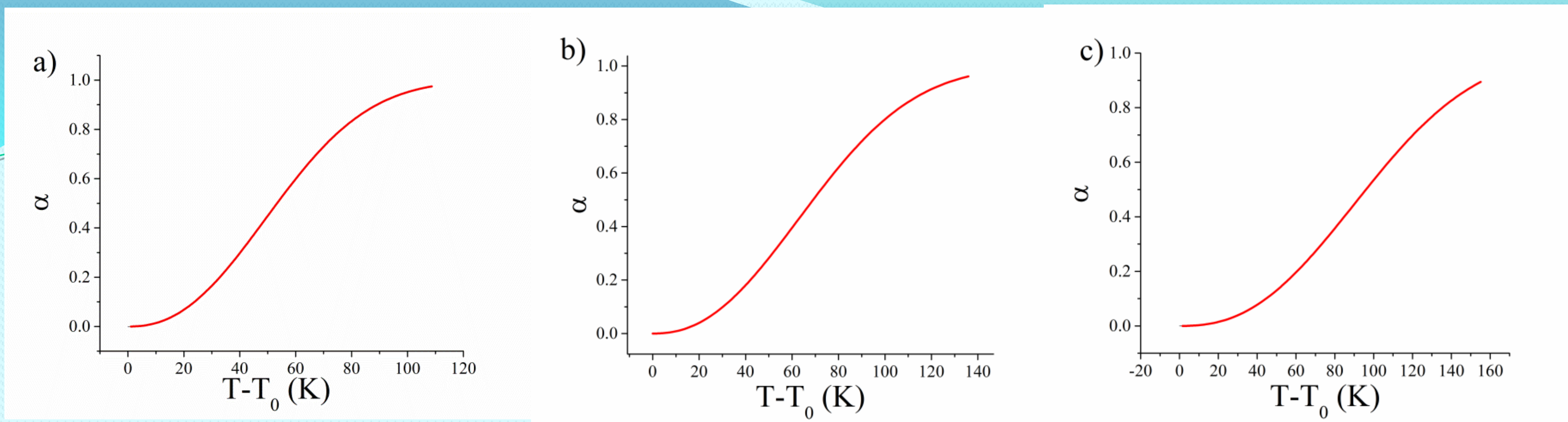


Figure 9. Nonlinear fitting of the Weibull function for equilibrium swallen PAAG hydrogel at different heating rate: a) 5K/min, b) 10K/min and c) 20K/min

Table 6. Comparison of the Weibull parameters at different heating rates, obtained by linear and nonlinear fitting for equilibrium swallen PAAG hydrogel

	Linear fitting		Non-linear fitting	
Heating rate $v_h(K/min)$	β	η	β	η
5	$2{,}91 \pm 0{,}01$	$13{,}15 \pm 0{,}01$	2,34	12,47
10	$2{,}87 \pm 0{,}02$	$7{,}04 \pm 0{,}01$	2,28	8,11
20	$2{,}93 \pm 0{,}02$	$4{,}37 \pm 0{,}01$	2,45	5,57

Table 7. Comparison of the Weibull parameters at different heating rates, obtained by linear fitting conversion curves for different swelling degrees of PAAG hydrogel

	(1:1) PAAG		(1:10) PAAG		Equilibrium swollen PAAG	
Heating rate $v_h(K/min)$	β	η	β	η	β	η
5	$2,28 \pm 0,01$	$13,68 \pm 0,01$	$2,68 \pm 0,01$	$13,54 \pm 0,01$	$2,91 \pm 0,01$	$13,15 \pm 0,01$
10	$2,28 \pm 0,01$	$7,72 \pm 0,01$	$2,79 \pm 0,01$	$7,38 \pm 0,01$	$2,87 \pm 0,02$	$7,04 \pm 0,01$
20	$2,27 \pm 0,01$	$4,71 \pm 0,01$	$2,92 \pm 0,01$	$4,65 \pm 0,01$	$2,93 \pm 0,02$	$4,37 \pm 0,01$

- The values of the parameter β at all investigated heating rate increase when the value of swelling degree increase.

- The values of the parameter η at all investigated heating rate decrease when the value of swelling degree increase.

Table 8. Comparison of the Weibull parameters at different heating rates, obtained by non-linear fitting conversion curves for different swelling degrees of PAAG hydrogel

	(1:1) PAAG		(1:10) PAAG		Equilibrium swollen PAAG	
Heating rate $v_h(K/min)$	β	η	β	η	β	η
5	1,42	14,79	1,96	13,06	2,34	12,47
10	1,73	9,11	2,22	8,37	2,28	8,11
20	1,64	5,88	2,48	5,79	2,45	5,57

Conclusions:

- It was found, that the Weibull distribution function of reaction times can successfuly describe the dehydration conversion curves at different heating rates.

- Both examined ways of fitting non-isothermal conversion curves of dehydration of PAAG hydrogel allow fitting of experimental conversion curves.

- The value of the parameter η at all indicated swelling degrees and heating rates is higher when applying non-linear regression analysis than the corresponding value for linear regression analysis while the parameter β has lower values .

- The values of the parameter η at all investigated swelling degrees decrease when the value of the heating rate increase.

- The values of the parameter β are complexly changed with the increase of heating rate.

- In both cases, when we applied linear or non-linear regression method, when swelling degree increases at an identical heating rate, the values of the parameter β increase, and the values of the parameter η decrease.

- The lower quality of fitting in the case of applying the linear regression method is a consequence of the double logarithm applied in this method, which results in an unrealistic increase in the value of the function parameters.

- Changes in the values of parameters β and η with the swelling degrees and the heating rate during the dehydration of PAAG hydrogel indicate a change in the state of absorbed water.

Thank you for your attention!