

Kinetic Parameters of the Cross-linking Reaction of Cellulose Membranes with Bifunctional Epoxides

Dominik Ruhr^{1,2,*} and Annette Reiche²

DOI: 10.1002/cite.202100088

 This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Kinetic parameters of the cross-linking reaction of porous cellulose membranes with aqueous solutions of two different diglycidyl ethers were determined by dynamic DSC experiments. The autocatalytic reaction behavior was described with an extended Prout-Tompkins equation. Kinetic analysis revealed a similar kinetic behavior for both diglycidyl ethers, with an apparent activation energy of 45–65 kJ mol⁻¹ and a reaction order between 0.9 and 1.5, suggesting a transition from one to another dominant reaction mechanism when the composition of the cross-linking solution is changed. Conversion curves based on the kinetic analysis serve as a basis for the design and optimization of a continuously running process for the industrial-scale production of cross-linked cellulose membranes.

Keywords: Cellulose membranes, Cross-linking, Differential scanning calorimetry, Epoxides, Kinetics

Received: May 31, 2021; *revised:* October 10, 2021; *accepted:* December 13, 2021

1 Cross-Linking of Cellulose Membranes with Bifunctional Epoxides

Because of their low tendency towards protein adsorption resulting in a minimal fouling behavior, porous membranes based on regenerated cellulose are widely used for filtration and purification applications in biopharmaceutical downstream processing [1, 2]. Due to the intrinsic hydrophilicity of cellulose and its extraordinary supramolecular structure caused by very strong hydrogen bonds, these membranes do not need any pretreatment before use and are highly compatible with many organic solvents.

Despite of all these beneficial properties, cellulose membranes exhibit a lack of dimensional stability in terms of swelling and shrinking during wetting and drying processes, which may jeopardize the integrity of the filtration unit such as a cartridge or a capsule. Furthermore, cellulose is prone to chemical degradation under strongly acidic or strongly alkaline conditions [3, 4], the latter ones often being applied in backwashing processes to recover the membrane surface.

In order to control these drawbacks, cellulose membranes often are chemically cross-linked, forming a three-dimensional polysaccharide network. A common industrial approach is the cross-linking of solid cellulose membranes in alkaline solutions containing water-soluble diglycidyl ethers such as 1,4-butanediol diglycidyl ether (BDDE) or poly(ethylene glycol) diglycidyl ether (PEGDE) [5]. During the cross-linking reaction stable covalent ether linkages with cellulose are formed (Fig. 1), enhancing the chemical,

thermal and mechanical resistance as well as the dimensional stability of the membrane.

Aside from formation of true chemical cross-links, the cross-linking of cellulose under these reaction conditions is accompanied by various side reactions such as alkaline hydrolysis of the epoxide groups, oligomerization reactions, or formation of incomplete cross-links resulting in a cellulose network bearing pendant epoxide groups [6, 7]. Although detailed investigation of these side reactions is very challenging, e.g., due to the similarity of the chemical bonds formed during cross-linking, it could recently be shown by ¹H NMR measurements that usually only half of the cross-linker molecules form true chemical cross-links while the other half forms loose ends in the polysaccharide network [6].

Additionally, the well-established manufacturing process currently used for the industrial production of cross-linked cellulose membranes is very time consuming. In this discontinuous batch process, cellulose membranes are impregnated in an alkaline aqueous solution containing the bifunctional epoxides and then are cross-linked for up to several days at room temperature [5]. In order to satisfy the

¹Dominik Ruhr
dominik.ruhr@sartorius.com
Leibniz University Hannover, Institute of Technical Chemistry,
Callinstraße 5, 30167 Hannover, Germany.

²Dominik Ruhr, Dr. rer. nat. habil. Annette Reiche
Sartorius Stedim Biotech GmbH, August-Spindler-Straße 11, 37079
Göttingen, Germany.

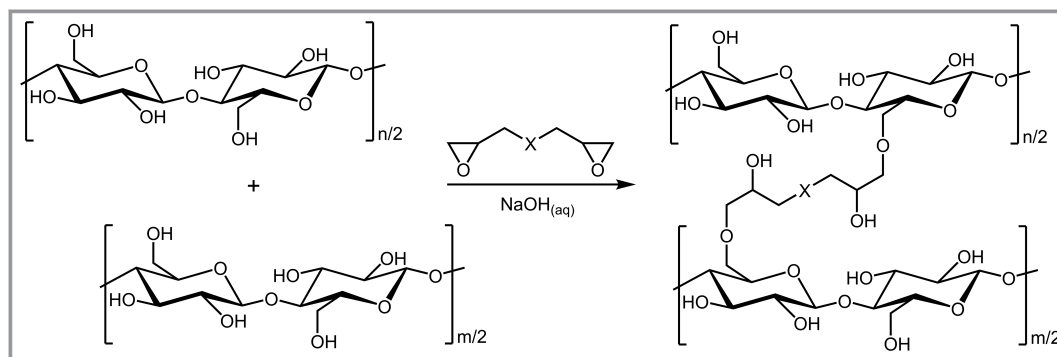


Figure 1. Targeted cross-linking reaction of cellulose with bifunctional epoxides under alkaline reaction conditions with n and m representing the number of anhydroglucose repeating units. $X = -O-(CH_2)_4-O-$ for BDDE and $X = -[O-(CH_2)_2]_j-O-$ for PEGDE, with j representing the number of ethylene glycol repeating units.

increasing demand for these filtration membranes while reducing production costs and time, a changeover from a batch-based process towards a continuous cross-linking process became necessary. Increasing the cross-linking temperature reduces the reaction time and thus allows a continuous processing of the membranes where a sufficient degree of cross-linking can be accomplished within a couple of minutes [8]. Reaction temperatures, however, should be kept as moderate as possible to prevent a thermal degradation of the membrane [8, 9].

Besides drastically increasing the production speed, the advantages of the continuous cross-linking process also include a general improvement of product quality and process consistency by production of more homogeneous membranes due to an enhanced control of processing conditions. Furthermore, less cross-linking agent is required to achieve a sufficiently high degree of cross-linking and the choice and tuning of process conditions allow to control the network density and the selectivity of the reaction by decreasing the amount of unwanted side reactions [8, 9].

1.1 Evaluation of Kinetic Parameters from Dynamic DSC Measurements

In order to design such a continuous cross-linking process and to find appropriate reaction conditions for the heterogeneous two-phase system a detailed kinetic analysis of the cross-linking reaction is required, especially regarding the composition of the cross-linking solution in terms of concentration of cross-linking agent and catalyst. It was shown in a previously published paper that this kinetic examination can be performed based on dynamic DSC experiments assuming that the degree of conversion is proportional to the area of the exothermal peak of the cross-linking reaction [7, 10]. The obtained data can be pre-evaluated with model-free methods such as Friedman analysis or Ozawa-Flynn-Wall analysis. Under formal assumption of first-order kinetics, both methods yield the activation energy E_A and the pre-exponential factor A known from the Arrhenius

equation as a function of the degree of conversion as well as the information whether the reaction is of retarding, accelerating or indifferent character. Based on this initial information, a suitable kinetic model can be fitted to the experimental data. A very comprehensive description of the theoretical background is provided, e.g., by [10] or [11], and an overview of the evaluation of the kinetic parameters of the system at hand using this experimental approach was already provided in [7].

It was found that the cross-linking reaction of cellulose membranes with diglycidyl ethers follows an autocatalytic behavior, which can be described properly by use of the extended Prout-Tompkins equation given in Eq. (3) in the experimental section. It was also observed that the curing reaction of a pure cross-linking solution in absence of a cellulose membrane exhibits very similar kinetic parameters at high concentrations of the cross-linking agent [7], indicating that the side reactions such as hydrolysis or oligomerization always play a major role in this reaction system. When evaluating the cross-linking kinetics based on dynamic DSC measurements, all possible reaction paths including all side reactions will take place simultaneously. As a result, the kinetic analysis only provides average or apparent kinetic parameters and thus delivers a formal description of the reaction. This, however, does not pose a problem since these apparent kinetic parameters are well-suited to formally describe the overall reaction sufficiently.

The aim of this study is to continue and complement the initial work published in [7] and to provide a detailed evaluation of the apparent kinetic parameters of the cross-linking reaction of solid cellulose membranes and two different bifunctional epoxides. For this purpose, several compositions of the cross-linking solution in a concentration range relevant for the continuous production process were tested and the respective kinetic parameters were evaluated.

2 Experimental

2.1 Preparation of Cross-Linking Solutions

The aqueous cross-linking solutions contained either BDDE (202 g mol⁻¹, Sigma Aldrich, technical grade) or PEGDE (Raschig, $M_w \approx 520$ g mol⁻¹, technical grade) as cross-linking agents and sodium hydroxide as a catalyst. A mass ratio of dried cellulose membrane and cross-linking solution of 1:8 was prepared in each DSC crucible. All solutions were freshly prepared before each measurement and covered a concentration of cross-linker between ca. 0.2 and 1.2 mol per kg of cross-linking solution and a molar ratio r of cross-linking agent and catalyst NaOH between 1.65 and 6.60. Aqueous solutions containing cross-linker concentrations below 0.2 mol kg⁻¹ or with a molar ratio higher than described above usually resulted in very low DSC signals so that these curves could not be simulated. Cross-linker concentrations above 1.2 mol kg⁻¹ or molar ratios lower than mentioned often yielded inhomogeneous cross-linking solutions leading to inaccurate DSC curves. For this study, only homogenous cross-linking solutions were used.

2.2 DSC Analysis of Cross-Linking Reaction of Cellulose with Bifunctional Epoxides

The method used in these experiments and typical DSC curves obtained from the measurements were already described and shown in detail in [7], therefore no additional DSC curves obtained in this study will be displayed here. For the dynamic DSC measurements performed in the context of this work, heating rates of 2.5, 5.0 and 10 K min⁻¹ were used. Raw data were processed with Netzsch Proteus software (version 7.1), baseline interpolation was accomplished using a Bézier curve. All simulations were performed with Netzsch Thermokinetics software (version 3.1).

2.3 Determination of Kinetic Parameters

Here, only a brief representation of the equations and kinetic models relevant for this work can be provided. Comprehensive descriptions of the theoretical background can be found in [10–12]. In this study, a model-free kinetic analysis according to Friedman was applied. Assuming an Arrhenius-like kinetic behavior with a pre-exponential factor $A(x)$ and an activation energy $E_A(x)$, complemented by an initially unknown reaction model $f(x)$, the reaction rate dx/dt depends on conversion x and is described according to Eq. (1) with R and T denoting the universal gas constant and the temperature, respectively:

$$\frac{dx}{dt} = A(x)f(x)\exp\left(-\frac{E_A(x)}{RT}\right) \quad (1)$$

Plotting of $\ln(dx/dt)$ against $1/T$ at a constant degree of conversion x (so-called Friedman diagram) yields a linear function with a slope of $-E_A/R$ and a y -intercept of $\ln(A(x)) + \ln(f(x))$ (Eq. (2)):

$$\ln\left.\frac{dx}{dt}\right|_x = \ln A(x) + \ln f(x) - \frac{E_A}{R} \frac{1}{T} \quad (2)$$

Assuming a first-order reaction where $\ln(f(x))$ equals zero, repetition of this procedure at different degrees of conversion finally yields a plot of pre-exponential factor A and activation energy E_A as a function of conversion x . Based on these initial values, a suitable reaction model $f(x)$ can be chosen to fit the simulated curves to the experimental data, turning the initially model-free kinetic analysis into a model-based kinetic analysis. It was previously shown in [7] and [9] that the reaction kinetics of the present reaction system can be described best with the extended form of the Prout-Tompkins equation as reaction model $f(x)$ for $x > 0$ (Eq. (3)):

$$f(x) = (1-x)^n x^a \quad (3)$$

In this reaction model, the parameters n and a represent the reaction order and the grade of autocatalysis, respectively. It should be noted that once a reaction model is chosen, all kinetic parameters (E_A , A , n , a , reaction enthalpy ΔH_R) are assumed to be constant while the reaction progresses. For this reason, an increasing or decreasing activation energy or pre-exponential factor cannot be considered.

3 Results and Discussion

All dynamic DSC measurements were processed as described in [7] under consequent use of an extended Prout-Tompkins equation as reaction model $f(x)$. Thus, all four apparent kinetic parameters required to simulate the measured data, i.e., activation energy E_A , pre-exponential factor A , reaction order n and grade of autocatalysis a , were evaluated the same way. Their dependence on the composition of the cross-linking solution is depicted as contour plots in Figs. 2 and 3 for BDDE and PEGDE as cross-linking agent, respectively. Unfortunately, the software used for the simulations provides an error estimation only for the activation energy, therefore errors are estimated by the authors to be $\Delta E_A = \pm 2$ kJ mol⁻¹, $\Delta \log(A/s^{-1}) = \pm 0.2$, $\Delta n = \pm 0.1$ and $\Delta a = \pm 0.05$ for each determination.

Since the accessible range of concentrations yielding reliable DSC signals was limited due to solubility or very low signal intensity, the concentration limits investigated in this study had to be slightly adjusted for each cross-linking agent. For this reason, some edges of the contour plots in the low (Fig. 2) or high (Fig. 3) concentration limit could not be measured or simulated and had to remain blank. Nevertheless, clear trends could be observed for each cross-linking agent.

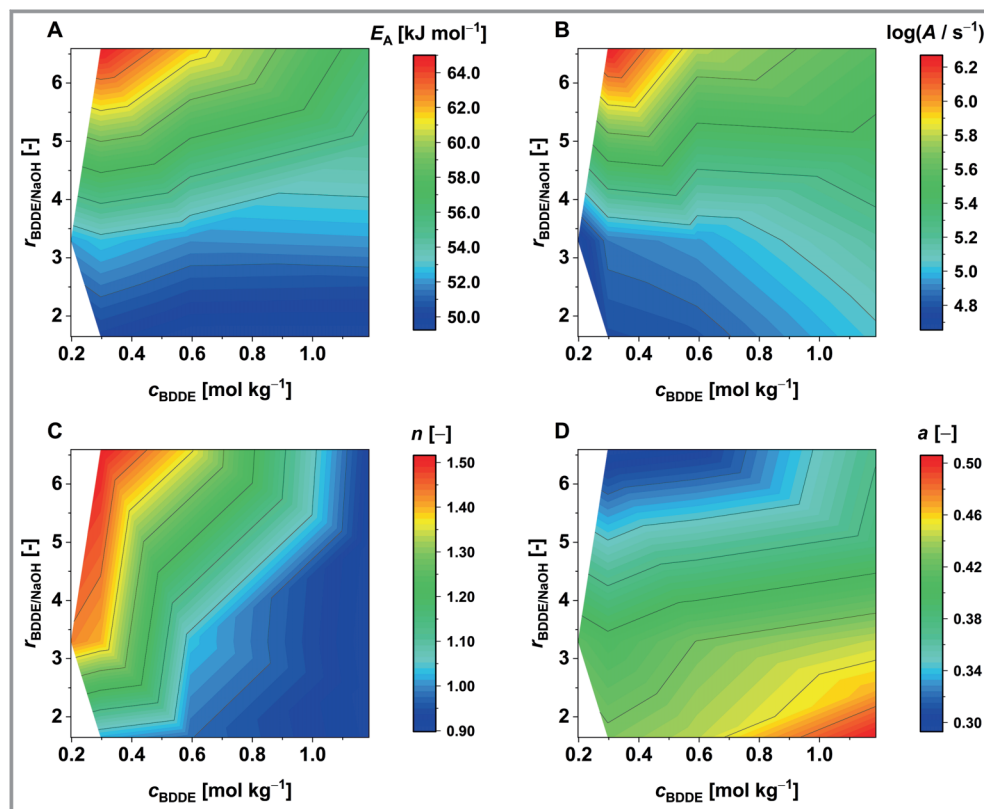


Figure 2. Dependence of apparent activation energy E_A (A), pre-exponential factor A (B), reaction order n (C) and grade of autocatalysis a (D) on BDDE concentration and molar ratio of BDDE and NaOH in the cross-linking solution for the cross-linking of cellulose with BDDE.

Because the investigated reaction system is equal for both cross-linking agents used in this study, the influence of the composition of the cross-linking solution on each apparent kinetic parameter will be discussed simultaneously for both cross-linking agents in the following sections.

3.1 Influence on Activation Energy

According to the simulations, the overall reaction of cellulose membranes with bifunctional epoxides exhibits an apparent activation energy E_A between ca. 45 and 65 kJ mol^{-1} for the diglycidyl ethers and compositions investigated in this study (Fig. 2A, Fig. 3A). It is only slightly influenced by the concentration of the cross-linking agent, but strongly influenced by the molar ratio of cross-linking agent and catalyst, i.e., the pH value. The highest activation energy is reached at low concentrations of both cross-linking agent and catalyst. Vice versa, high concentrations of both cross-linking agent and catalyst lead to lowest activation energies.

Furthermore, comparison of the activation energies of the cross-linking agent with a short backbone (BDDE, Fig. 2A) and the cross-linking agent with a longer backbone (PEGDE, Fig. 3A) suggests a very similar reactivity in terms of activation energies. Although reactions involving PEGDE

as cross-linking agent exhibit slightly smaller activation energies compared to BDDE as cross-linker it is not clear whether these differences can be attributed to a higher chain flexibility or to the experimental error of the simulations. Since the actual differences are rather small, the activation energies can be regarded as equal, and it can be concluded that the chain-length of the cross-linking agents used in this study does not have a significant effect on the general reactivity. However, it should be noted that the reactivity of cross-linking agents with even longer backbones may be influenced to a larger extent by steric or diffusional reasons and therefore may show a different behavior compared to the cross-linking agents investigated in this study.

In Figs. 2A and 3A it can be seen that high catalyst concentrations lead to activation energies around 50 kJ mol^{-1} . While these values are typical of many homogenous reactions in solution [13], an increasing activation energy might indicate a transition towards another dominant reaction mechanism emphasizing the competing character between the targeted heterogenous cross-linking reaction of cellulose hydroxyl groups (Fig. 1) and side reactions of the cross-linker such as hydrolysis and homopolymerization that take place in the homogenous cross-linking solution. As these side reactions cannot be avoided, the apparent activation energy will always be an average value of these different

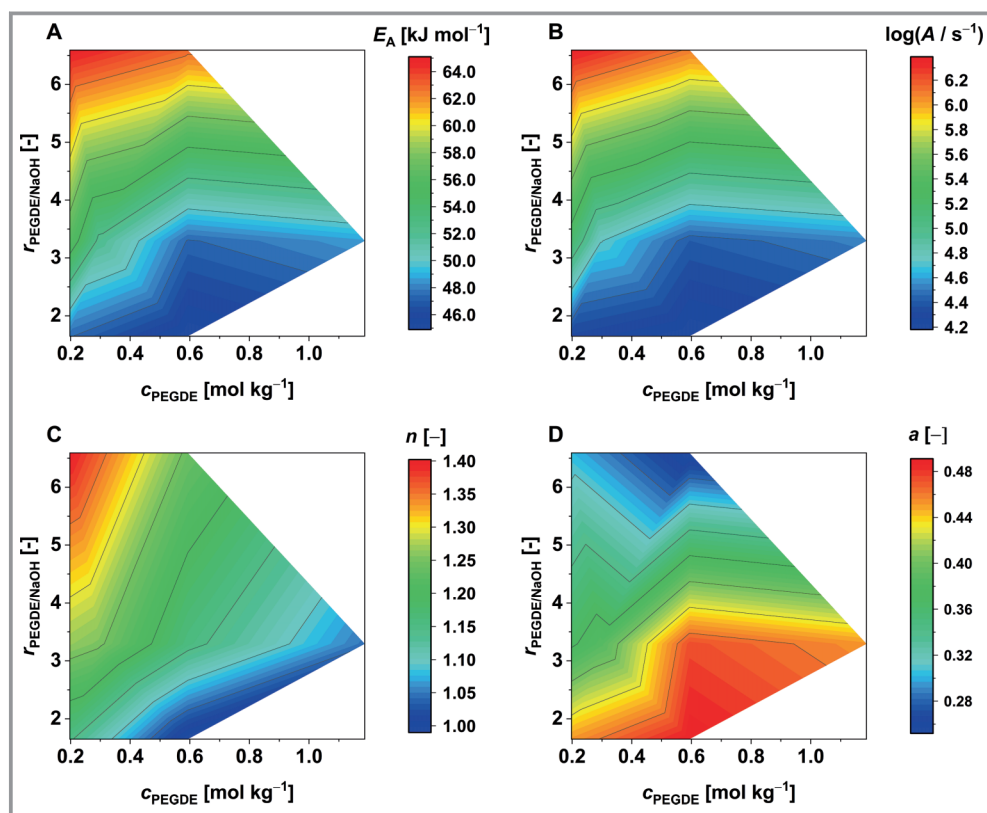


Figure 3. Dependence of apparent activation energy E_A (A), pre-exponential factor A (B), reaction order n (C) and grade of autocatalysis a (D) on PEGDE concentration and molar ratio of PEGDE and NaOH in the cross-linking solution for the cross-linking of cellulose with PEGDE.

contributions. Despite of this drawback, a clear trend of the apparent activation energy can be observed for both cross-linking agents.

In general, both an increasing concentration of the cross-linker at a constant molar ratio of cross-linking agent and catalyst NaOH in the cross-linking solution and an increase of the catalyst amount at a constant concentration of cross-linking agent lower the apparent activation energy. The effect of the catalyst concentration, however, is stronger compared to a variation of cross-linker concentration in solution because a significantly higher pH not only facilitates the nucleophilic attack of cellulose hydroxyl groups on the epoxide groups, but also increases the rate of ring-opening of the epoxide groups by alkaline hydrolysis. It was also observed that the impact of the catalyst concentration is stronger at low cross-linker concentrations and becomes less important for high concentrations of cross-linking agent (Fig. 2A). This effect generally also was observed for all high catalyst concentrations and indicates an increasing proportion of side reactions in solution when the amount of cross-linker or catalyst is increased. In order to diminish these side reactions and enhance the proportion of actual reaction with cellulose hydroxyl groups, the cross-linking reaction hence should not only be conducted at low concentrations of cross-linking agents, but also the amount of catalyst should be kept as low as possible.

Although reactions of cellulose and diglycidyl ethers had been intensively examined in the 1960s in the context of crease recovery of cotton clothing [14–18], no kinetic data on these reactions have been reported so far and comparison with literature values therefore turned out to be difficult. Nevertheless, the apparent activation energies found in this study are in good agreement with those reported by Rodríguez et al. [19] who investigated the cross-linking of cationic hydroxyethyl cellulose hydrogels with ethylene glycol diglycidyl ether, the monomeric homologue of PEGDE. Depending on the molecular structure of the hydroxyethyl cellulose, they found apparent activation energies around 70–90 kJ mol⁻¹ as determined by rheometric analysis. The composition of the cross-linking solutions used in their work was comparable to those investigated in the study at hand. Interestingly, they found a lower activation energy when the amount of cross-linking agent was increased. A similar behavior could also be observed for the cross-linking of cellulose with PEGDE when the cross-linking solutions contained low concentrations of the cross-linker (Fig. 3A). Although the same behavior can be assumed for BDDE as cross-linking agent (Fig. 2A), no evidence was found in this study since cross-linking solutions containing such low BDDE concentrations did not yield sufficiently strong DSC signals that could be used for simulations.

3.2 Influence on Pre-Exponential Factor

It can be observed from all simulations that the apparent pre-exponential factor $\log(A)$ for both BDDE (Fig. 2B) and PEGDE (Fig. 3B) follows similar trends as described for the respective apparent activation energy, especially in case of PEGDE. Whenever the activation energy rises, the pre-exponential factor does likewise. Although increasing the relative amount of catalyst was expected to increase the proportion of collisions leading to a successful reaction, the contrary was observed. The less catalyst in the cross-linking solution, the higher the observed apparent pre-exponential factor. This, however, does not automatically yield a faster overall reaction rate since it should be kept in mind that the reaction rate is a combination of all four kinetic parameters (Eq. (1)).

A possible explanation for this kinetic behavior might be an electrostatic repulsion. High amounts of hydroxide ions in solution lead to an increased amount of deprotonated cellulose hydroxyl groups as well as hydrolyzed epoxide groups in solution. Although the number of “active” sites at the cellulose chains might be large, electrostatic repulsions between deprotonated hydroxyl groups of cellulose or hydrolyzed epoxide groups may possibly inhibit further reactions of cross-linker molecules with cellulose. Just like observed for the apparent activation energy, in case of BDDE the influence on $\log(A)$ when varying the molar ratio of cross-linking agent and catalyst apparently is more pronounced at lower concentrations of cross-linking agent since a transition of the pre-dominant reaction mechanism is more visible when side reactions in solution are suppressed. For high BDDE concentrations, however, side reactions in solution apparently always play a dominant role so that the actual cross-linking reaction is heavily distracted or superimposed.

Compared to BDDE, very similar trends can also be observed for PEGDE as cross-linking agent, with the apparent pre-exponential factor $\log(A)$ exactly following the same trends as described for the activation energy (Fig. 3B). Nevertheless, in case of PEGDE the pre-exponential factor seems to be less dependent on the cross-linker concentration compared to BDDE and also seems to remain almost constant when the cross-linker concentration is further increased, which means that a cross-linking system containing PEGDE as cross-linking agent might be less sensitive to small pH changes.

3.3 Influence on Reaction Order

The simulations suggest that a steady transition of the apparent reaction order n can be observed when the concentration of the cross-linker is increased or when the ratio of cross-linker to catalyst is changed (Figs. 2C, 3C). High cross-linker concentrations and high proportions of catalyst yield a nearly first-order reaction for both BDDE and PEGDE, which is in agreement with the reaction order found by Rodríguez et al. [19]. However, low concentrations

of cross-linking agent and catalyst exhibit a higher apparent reaction order suggesting a transition from one to another pre-dominant reaction mechanism. While a first-order reaction can be attributed to a high proportion of side reactions of the epoxide groups in solution, a reaction of higher order might be an indicator for the targeted reaction of epoxide groups with hydroxyl groups of cellulose. This is already known from the very similar curing reaction of epoxy with amine hardeners where often reaction orders between 1.5 and 2 are observed for the second reaction step [20].

In order to verify this assumption, further DSC experiments with cross-linking solutions in absence of a cellulose membrane were performed. In these experiments, cross-linking solutions containing BDDE were measured. While the BDDE concentration was kept constant at 0.3 mol kg^{-1} , the molar ratio of BDDE and NaOH was varied between 1.65 and 6.60. According to the respective simulations, activation energies between 45 and 50 kJ mol^{-1} , pre-exponential factors $\log(A)$ between 4.0 and 4.4, and a constant reaction order of 1.0 was observed. Thus, it can be concluded that an increasing reaction order indeed can be attributed to the reaction with cellulose hydroxyl groups.

Finally, comparison of apparent reaction order, activation energy and pre-exponential factor shows that all of these kinetic parameters only change slightly in the high-concentration region in terms of cross-linker concentration, confirming the assumption that side reactions in solution always play the pre-dominant role once the cross-linking solution contains too high amounts of cross-linking agents or catalyst.

3.4 Influence on Grade of Autocatalysis

The simulations indicate an increasing grade of autocatalysis (exponent a) when the concentration of cross-linker or catalyst is increased (Figs. 2D, 3D). According to Eq. (1), exponent a describes the acceleration of the reaction rate by the reaction products, thus a transition from low to high values also reflects an increasing rate of autocatalysis. Higher concentrations of BDDE or PEGDE and thus an increase in pH leads to a higher degree of autocatalysis, an effect also observed when the amount of catalyst is increased at a constant concentration of cross-linking agent. This behavior can be attributed to an increasing amount of hydroxyl groups available after hydrolysis of epoxide groups. From comparison of the trends for both BDDE and PEGDE it can be concluded that both systems show a very similar autocatalytic behavior under equal reaction conditions.

3.5 Application in the Continuous Production of Cross-Linked Cellulose Membranes

The kinetic parameters obtained from these experiments are supposed to serve as a basis for the design and optimization

tion of an industrial process used for the continuous production of cross-linked cellulose membranes. In order to explain how the obtained results can be applied in the industrial manufacturing process, conversion curves for the reaction of cellulose membranes with cross-linking solutions containing BDDE (0.3 mol kg^{-1}) and different amounts of catalyst were simulated by use of Euler's method (step size $\Delta t = 0.9 \text{ s}$) for a hypothetical reaction time of 15 min at a reaction temperature of $100 \text{ }^\circ\text{C}$ (Fig. 4).

The performed simulations clearly show the strong influence of the catalyst concentration in the cross-linking solution on the reaction kinetics. While reaction of cellulose with a cross-linking solution containing a high amount of catalyst yields a conversion of nearly 100% under given reaction conditions, a decreasing catalyst concentration clearly leads to lower degrees of conversion. Since the degree of conversion is equivalent to the amount of epoxide groups that reacted in one or another way, a high degree of conversion represents a high amount of epoxide groups that will have either reacted with cellulose hydroxyl groups to form ether linkages and cross-links or that have been hydrolyzed in unwanted side reactions. A cellulose membrane cross-linked under these conditions therefore will not have any pendant epoxide groups left. Reducing the amount of catalyst, however, results in a partially cross-linked cellulose network carrying pendant epoxide groups that can readily be used for further surface modifications.

4 Conclusion

In this study, comprehensive sets of kinetic parameters of the cross-linking reaction of solid cellulose membranes with two water-soluble diglycidyl ethers were determined by DSC and the reaction kinetics were modeled with the extended form of the Prout-Tompkins equation.

Results suggest that both a cross-linking agent with a short backbone (BDDE) and one with a long backbone (PEGDE) show comparable reactivity and that their respective reaction with cellulose can be described with a similar set of kinetic parameters. Depending on the exact composition of the aqueous cross-linking solution, an activation energy between 45 and 65 kJ mol^{-1} , a pre-exponential factor $\log(A)$ between 4 and 7 , a reaction order between 1 and 1.5 , and a grade of autocatalysis between 0.25 and 0.5 were observed. These values slightly differ from respective kinetic parameters determined under same reaction conditions in absence of a cellulose membrane, especially a reaction order >1 clearly indicates a reaction of the epoxide groups with the hydroxyl groups of cellulose.

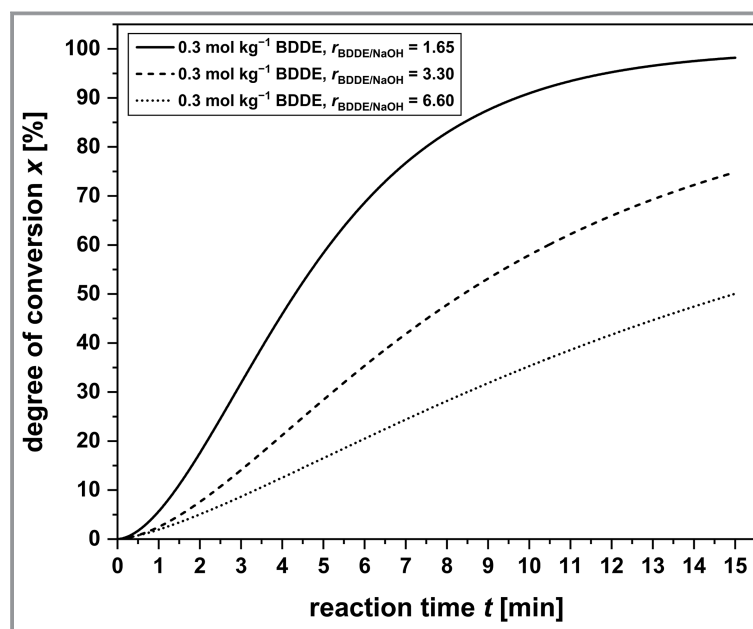


Figure 4. Conversion curves for the reaction of cellulose membranes with BDDE for different compositions of the cross-linking solution. Simulations performed for a reaction temperature of $100 \text{ }^\circ\text{C}$.

Additionally, it was found that high amounts of cross-linking agents and catalyst in the cross-linking solution led to high proportions of side reactions such as hydrolysis or oligomerization. In order to reduce the amount of these unwanted side reactions and push the reaction system towards the reaction with cellulose hydroxyl groups it is recommended to conduct the cross-linking reaction at low concentrations of cross-linking agents and moderate amounts of catalyst.

Finally, the sets of kinetic parameters for each cross-linking agent and the trends gained in this study can be used as a reliable base to precisely design and optimize an industrial process for the continuous production of cross-linked cellulose membranes.

Open access funding enabled and organized by Projekt DEAL.

Symbols used

a	$[-]$	grade of autocatalysis
A	$[\text{s}^{-1}]$	pre-exponential factor
c	$[\text{mol kg}^{-1}]$	concentration
E_A	$[\text{kJ mol}^{-1}]$	activation energy
ΔH_R	$[\text{kJ mol}^{-1}]$	reaction enthalpy
M	$[\text{g mol}^{-1}]$	molar mass
n	$[-]$	reaction order
r	$[-]$	molar ratio
R	$[\text{J mol}^{-1}\text{K}^{-1}]$	universal gas constant

t	[s]	time
T	[K]	temperature
x	[-]	degree of conversion

Abbreviations

BDDE	1,4-butanediol diglycidyl ether
DSC	differential scanning calorimetry
PEGDE	poly(ethylene glycol) diglycidyl ether

References

- [1] K.-V. Peinemann, S. P. Nunes, *Membranes for the Life Sciences*, Vol. 1, Wiley-VCH Verlag, Weinheim 2008.
- [2] S. Haindl, *Basic studies for sterile filtration processing of therapeutic protein formulations*, Ph.D. Thesis, Leibniz University Hannover 2020.
- [3] S. Wei, V. Kumar, G. S. Banker, *Int. J. Pharm.* **1996**, *142* (2), 175–181. DOI: [https://doi.org/10.1016/0378-5173\(96\)04673-X](https://doi.org/10.1016/0378-5173(96)04673-X)
- [4] C. J. Knill, J. F. Kennedy, *Carbohydr. Polym.* **2003**, *51* (3), 281–300. DOI: [https://doi.org/10.1016/S0144-8617\(02\)00183-2](https://doi.org/10.1016/S0144-8617(02)00183-2)
- [5] H. Beer, W. Demmer, H.-H. Hörl, D. Melzner, D. Nussbaumer, H.-W. Schmidt, E. Wünn, *Patent WO 95/32793*, 1995.
- [6] D. Ruhr, M. John, A. Reiche, *Carbohydr. Polym.* **2021**, *251* (1), 117043. DOI: <https://doi.org/10.1016/j.carbpol.2020.117043>
- [7] J. Tolk, D. Ruhr, A. Reiche, S. van der Kruijs, *Chem. Ing. Tech.* **2018**, *90* (7), 1011–1015. DOI: <https://doi.org/10.1002/cite.201700058>
- [8] S. van der Kruijs, A. Reiche, G. Niño-Amézquita, L. Villain, H.-H. Hörl, D. Melzner, F. Bäche, *Patent EP3490695 B1*, 2020.
- [9] J. A. Tolk, *Mikrofiltrationsmembranen auf Basis von regenerierter Cellulose*, Ph.D. Thesis, Leibniz University Hannover 2017.
- [10] N. Sbirrazzuoli, S. Vyazovkin, *Thermochim. Acta* **2002**, *388* (1–2), 289–298. DOI: [https://doi.org/10.1016/S0040-6031\(02\)00053-9](https://doi.org/10.1016/S0040-6031(02)00053-9)
- [11] K. Pielichowski, P. Czub, J. Pielichowski, *Polymer* **2000**, *41* (12), 4381–4388. DOI: [https://doi.org/10.1016/S0032-3861\(99\)00694-1](https://doi.org/10.1016/S0032-3861(99)00694-1)
- [12] I. V. Arkhangel'skii, A. V. Dunaev, I. V. Makarenko, N. A. Tikhonov, S. S. Belyaev, A. V. Tarasov, *Non-Isothermal Kinetic Methods*, Max Planck research library for the history and development of knowledge: Textbook series, Vol. 1, Edition Open Access, Berlin 2017.
- [13] H. Kuhn, H.-D. Försterling, D. H. Waldeck, *Principles of Physical Chemistry*, 2nd ed., John Wiley & Sons, Hoboken, NJ 2009.
- [14] J. B. McKelvey, B. G. Webre, E. Klein, *Textile Res. J.* **1959**, *29* (11), 918–925. DOI: <https://doi.org/10.1177/004051755902901111>
- [15] J. Galligan, A. M. Sookne, J. T. Adams Jr., H. Guest, G. H. Lourigan, *Textile Res. J.* **1960**, *30* (3), 208–222. DOI: <https://doi.org/10.1177/004051756003000306>
- [16] R. R. Benerito, B. G. Webre, J. B. McKelvey, *Textile Res. J.* **1961**, *31* (9), 757–769. DOI: <https://doi.org/10.1177/004051756103100901>
- [17] J. B. McKelvey, R. R. Benerito, B. G. Webre, R. J. Berni, *J. Polym. Sci., Part A: Polym. Chem.* **1961**, *51* (155), 209–230. DOI: <https://doi.org/10.1002/pol.1961.1205115513>
- [18] T. Francis, M. L. Staples, *Textile Res. J.* **1963**, *33* (8), 583–599. DOI: <https://doi.org/10.1177/004051756303300801>
- [19] R. Rodríguez, C. Alvarez-Lorenzo, A. Concheiro, *J. Control. Release* **2003**, *86* (2–3), 253–265. DOI: [https://doi.org/10.1016/S0168-3659\(02\)00410-8](https://doi.org/10.1016/S0168-3659(02)00410-8)
- [20] M. Boehm, *Reaction kinetics and cure monitoring of highly reactive epoxy resins for carbon fiber reinforced plastics*, Ph.D. Thesis, Ludwig Maximilian University of Munich 2015.