The Kinetics of Cellulose Grafting with Vinyl Acetate Monomer

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Abstract: Cellulose is a natural raw material recurring in a great quantity. The demand to use it more and more widely is increasing. The production of cellulose derivates started as early as the 19th century, however the modification of these materials meant the breaking up the fibrous structure, which made their use more difficult in paper industry. The modified cellulose made by graft copolymerization, however, keeps its fibrous character, which provides a great advantage regarding its use. Grafting of industrial cellulose pulp with vinyl-acetate allows for the production of grafted wood cellulose fibres that have a thermoplastic layer on their surface. The binder fibre (fibrid) produced in this way can be excellently used for producing synthetic papers.

In the first part of my experiments I dealt with choosing the parameters of graft copolymerization which are best suited to various uses and after that I studied the dependence of graft reaction on the composition and properties of industrial cellulose applied. The selection of the suitable reaction parameters was followed by the study of reaction speed and activation energy. I have stated that the gross reaction of grafting industrial cellulose with vinyl-acetate monomer is a second order reaction, which is proven by the fact that the invert of the momentary monomer concentration of the system plotted against time is a linear function. The rise of the curves, that is, the reaction speed increases when the temperature in the range of 293–323 K is increasing, while the average activation energy decreases.

Keywords: cellulose, copolymerization, vinyl acetate, reaction parameters, binder fibre, reaction speed, activation energy.

1   Introduction

The behaviour of paper made on a paper machine by planking the fibres – despite the development of ingredients used in paper industry – depends first of all on the physical and chemical properties of cellulose fibres. With the advance of paper-

synthetics combinations, however, several disadvantageous properties of paper due to the behaviour of fibres can be excluded.

There are two basic methods for the completion of paper-synthetics systems:

- the paper or cellulose is associated with finished synthetics or semi-finished synthetic products. Such products are: plywood paper, paper covered with plastics, paper coated with warmish, and paper treated on its surface or inside. For these combinations foil, latex, synthetic rosin hardening with heat, synthetic dispersions, synthetic solutions and synthetic hot-melts can be used.

- the other way to produce paper-synthetics systems is the modification of cellulose itself. This modification can be done by esterification, alkalization, nucleophil substitution, oxidation, or copolymerization.

As the cellulose itself has a polymer structure, it can only produce block or graft copolymers. The synthesis of cellulose block copolymers cannot be widely applied for the chemical modification of cellulose, since it essentially changes the physical structure of cellulose.

The chemical modification of cellulose fibre by graft copolymerization is of great importance because, by grafting a relatively small amount of monomers, this natural macromolecular material can be provided with a number of new advantageous properties. Graft copolymerization makes it possible to produce industrial cellulose fibres which can be successfully applied for making special, marked papers, and it can be also used as binder fibres of synthetic papers.

2   Background to the Research

Cellulose fibre is a natural raw material recurring in a great quantity. The demand to use it more and more widely is increasing. The production of cellulose by-products started as early as the 19th century, however the modification of these materials meant the breaking up the fibrous structure, which made their use more difficult in paper industry. The modified cellulose made by graft copolymerization, however, keeps its fibrous character, which provides a great advantage regarding its use.

Analysing the literature on the techniques of graft copolymerization, we can state that initiation by redox systems for initiating the reaction is the technique that can be carried out in the easiest way in industry. Among these techniques the best seems to be the one in which the role of a reducing component is acted by the cellulose itself, and the oxidizing component is a metal of changing valence.

In most cases the grafting reaction was carried out on regenerated cellulose pulp, fibres and films /1,2,3,4/. In some cases cellulose derivates, above all cellulose

esters and ethers were used. The high price of cellulose and cotton cellulose pulp makes it necessary that a cheaper industrial-technical cellulose fibre should be examined on its grafting ability. The grafting efficiency of industrial cellulose is affected, to a great extent, by the lignin left behind in the cellulose pulp during exploration or bleaching. This lignin acts as an inhibitor in the grafting reaction of the cellulose pulp, since it retards the formation of macro-radicals required for the beginning of grafting. According to the publications it was stated in the publications studied that the greater amount the lignin the greater the induction period of the reaction. /5,6/.

Few papers deal with the effect of the specific surface of the cellulose pulp on grafting /7,8/. I have found no papers dealing with the effects of the incrusting materials of industrial cellulose, the content and origin of hemi cellulose on graft copolymerization.

In Hungary experiments have been going on in the Research Institute of Paper Industry in connection with the grafting of cellulose pulp in paper industry, and experiments related to graft copolymerization in textile industry have been carried on in the Research Institute of Textile Industry, since 1966.

At the Paper Industry Department of the Technical College of Light Industry, which is the predecessor of the Budapest Tech, Rejtő Sándor Faculty of Light Industry, we have been dealing with grafting of industrial cellulose pulp with vinyl monomers since 1974.

3 Effect of Temperature, Reaction Time, Monomer - and Initiator Concentration, Liquor Ratio, and the Composition and Properties of Industrial Cellulose on Grafting Efficiency

In my first experiments I dealt with choosing the parameters of graft copolymerization which are best suited to various uses. Using an initiation method, which has already been studied in literature, that is using Ce(IV) salt, I grafted vinyl-acetate on bleached cellulose and examined the dependence of graft yield on the conditions of reaction, such as, temperature, reaction time, concentration of monomer and initiator, and liquor ratio /9/.

In the case of sulphate-cellulose fibre, which I examined, the reaction parameters of binder fibre, best suited to practical use are:

- temperature: 323 K

- reaction time: 40 minutes

- monomer concentration: 1 mol/dm^3

- initiator concentration: $2 \cdot 10^{-3}$ mol/dm^3

- liquor ratio: 100 cm^3/g cellulose

In the following part of my investigations I studied the dependence of graft reaction on the composition and properties of industrial cellulose applied. I examined the effect of the lignin content, hemi cellulose content and the specific surface of industrial cellulose on graft copolymerization.

I have stated that when grafting industrial cellulose with vinyl-acetate, a sufficient yield can be reached only if the lignin content of cellulose fibre is less than 2%. The hemi cellulose content of industrial cellulose fibre increases the yield of graft copolymerization, the grafting efficiency of the alpha cellulose obtained is lower than that of industrial cellulose containing hemi cellulose too. This can be explained by the greater reactivity and better availability of hemi cellulose. In the case of the examined reaction, the increase of the specific surface also increases – up to a given limit – the reaction yield. My experiments have shown that a further increase of the pulping time results in a decrease of yield because, in the case of an identical initiator concentration, while the specific surface rapidly increases, the number of radicals per unit surface decreases.

4 Study the Kinetics of Grafting Reaction

The selection of the suitable reaction parameters was followed by the study of reaction speed and activation energy /9/.

For studying the kinetics of grafting reaction I carried out the grafting at temperatures 293, 303, 313 and 323 K. The measured grafting efficiency is shown in Table I and Figure 1.

Reaction time (min) / Temperature (K)	293	303	313	323
5	1,98%	4,3%	6,5%	7,6%
10	4,5%	9,2%	16,4%	21,2%
20	9,3%	19,5%	36,9%	52,3%
30	22,6%	55,9%	108,9%	166,3%
40	36,2%	98,0%	181,7%	274,5%
60	61,9%	161,4%	253,1%	366,0%

Table I

Effect of reaction time and temperature on grafting efficiency
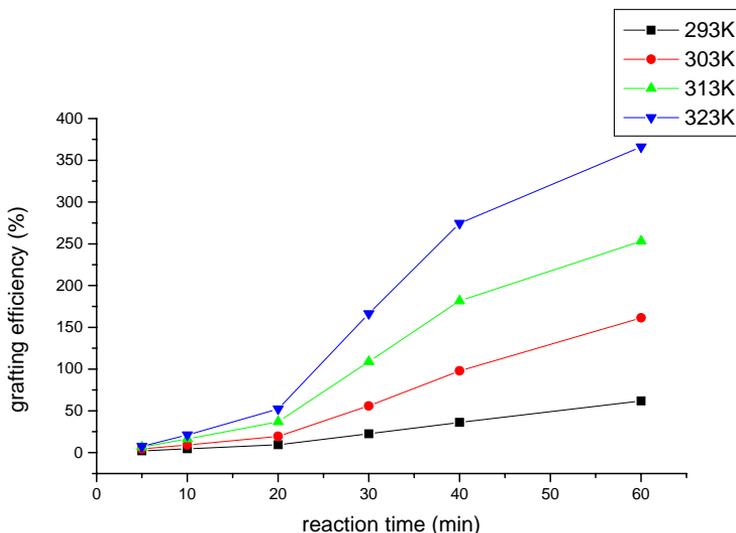
Figure 1

Effect of reaction time and temperature on grafting efficiency. Monomer concentration: 1,0 mól/dm^3, initiator concentration: 2.10^{-3} mól/dm^3, liquor ratio: 100 cm^3/g cellulose

From the results I calculated the average activation energy values for each temperature, using the Arrhenius equation (1), which is well suited to approximate calculations:

$$E = 2,3 \cdot R \cdot \frac{T_1 \cdot T_2}{T_2 - T_1} \cdot \lg \frac{k_2}{k_1} \qquad \text{(KJ/mol)} \tag{1}$$

where: T_1 = lower temperature (K)

T_2 = higher temperature (K)

k_1 = reaction speed constant at the lower temperature (mol/dm^3.min)

k_2 = reaction speed constant at the higher temperature (mol/dm^3.min)

The calculation of the reaction rate constants (2) is the following:

$$k_\tau = \frac{c_0 - c_\tau}{\tau \cdot c_0 \cdot c_\tau} \tag{2}$$

where: τ = reaction time (min)

c_0 = initial monomer concentration (mol/dm^3)

c_τ = monomer concentration after τ reaction time (mol/dm^3)

The results have shown that – according to my expectations – when the temperature increases, the average activation energy of the reaction decreases (Table II).

Reaction time (min)	T = 293-303 K (kJ/mól)	T = 303-313 K (kJ/mól)	T = 313-323 K (kJ/mól)
5	$E_5 = 57{,}2863$	$E_5 = 26{,}5167$	$E_5 = 21{,}1128$
10	$E_{10} = 55{,}2730$	$E_{10} = 24{,}4425$	$E_{10} = 23{,}0555$
20	$E_{20} = 58{,}9075$	$E_{20} = 47{,}7685$	$E_{20} = 26{,}0562$
30	$E_{30} = 63{,}4572$	$E_{30} = 57{,}9796$	$E_{30} = 41{,}8575$
40	$E_{40} = 78{,}7772$	$E_{40} = 58{,}2355$	$E_{40} = 41{,}8463$
60	$E_{60} = 79{,}1305$	$E_{60} = 58{,}9343$	$E_{60} = 46{,}4898$

Table II

The average activation energy values

As it has already been mentioned, the reaction goes on in a complicated heterogeneous system thus, apart from the kinetics of the chemical reaction, certain macro-kinetic factors affecting the rate of material transmission may also have an effect on the gross rate of the reaction. From the results of the experiments on parameters I have calculated the gross rate of the reaction in the range of 20–60 reaction time after the induction period (Figure 2, 3, 4, 5), and by analysing the curves, I have defined the equations for the changes of rate in time.

These are:

at temperature 293 K. $v = 2{,}32114 \cdot 10^{-5}\, t^2 - 0{,}00269\, t + 0{,}09354$

at temperature 303 K. $v = 2{,}45545 \cdot 10^{-5}\, t^2 - 0{,}00283\, t + 0{,}09528$

at temperature 313 K. $v = 2{,}66932 \cdot 10^{-5}\, t^2 - 0{,}00298\, t + 0{,}09543$

at temperature 323 K. $v = 3{,}04886 \cdot 10^{-5}\, t^2 - 0{,}00336\, t + 0{,}10166$
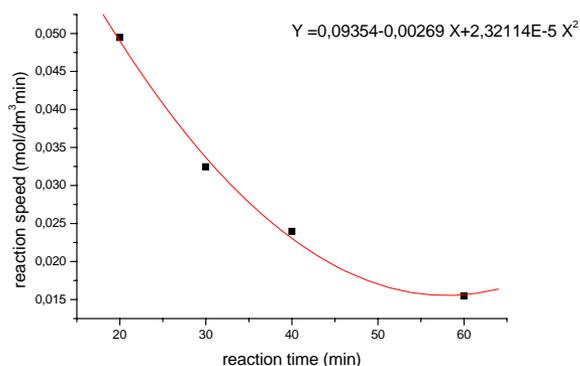
Figure 2

The change in reaction rate with increasing reaction time at temperature 293 K
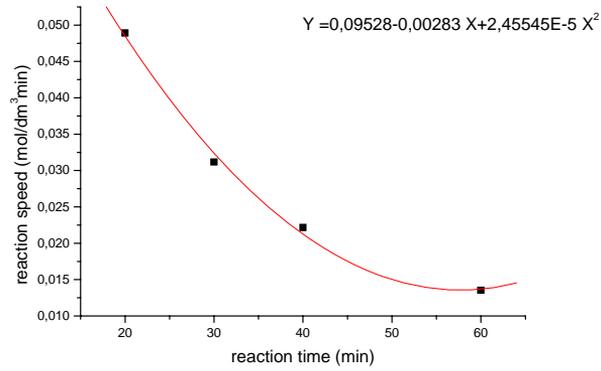
Figure 3

The change in reaction rate with increasing reaction time at temperature 303 K
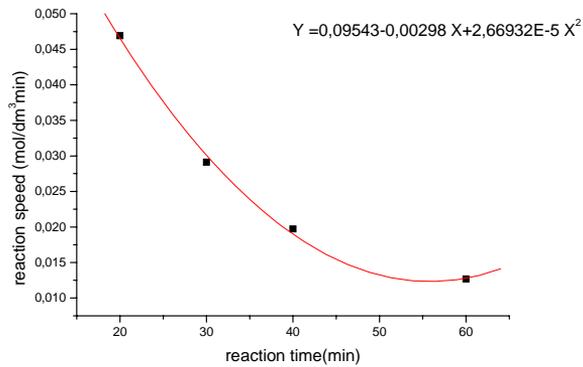
Figure 4

The change in reaction rate with increasing reaction time at temperature 313 K

$$Y = 0,10166 - 0,00336\,X + 3,04886E\text{-}5\,X^2$$
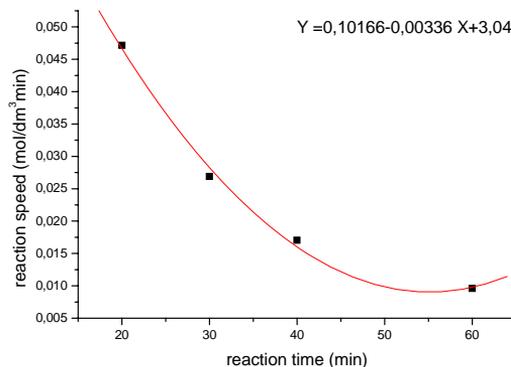
Figure 5

The change in reaction rate with increasing reaction time at temperature 323 K

When the invert of the momentary monomer concentration is plotted against reaction time, it can be stated that the function is a linear one at those four temperatures studied, which proves the fact that the gross reaction rate is a second order reaction (Figure 6, 7, 8, 9).
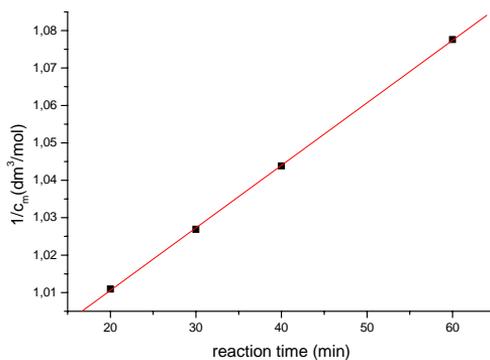
Figure 6

The change in the inverse of the momentary monomer concentration reaction with increasing reaction time at temperature 293 K

The equation for the change of rate in time at temperature 293 K:

$$Y = 0,97714\,(\pm\ 5,40641 \cdot 10^{-4}) + 0,00167\,(\pm\ 1,3412 \cdot 10^{-5})\,X \qquad R = 0,99994$$
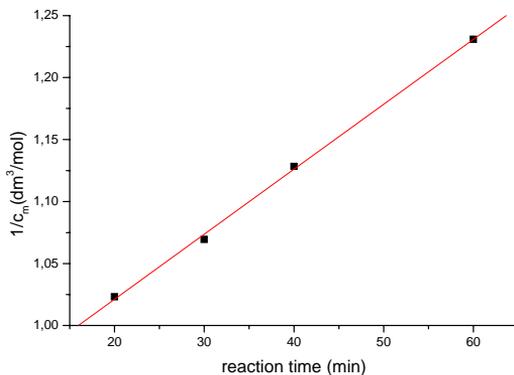
Figure 7

The change in the inverse of the momentary monomer concentration reaction with increasing reaction time at temperature 303 K

The equation for the change of rate in time at temperature 303 K:

$$Y= 0{,}9164\ (\pm\ 5{,}06\cdot10^{-3}) + 0{,}00524\ (\pm\ 1{,}2541\cdot10^{-4})\ X \qquad\qquad R = 0{,}99943$$
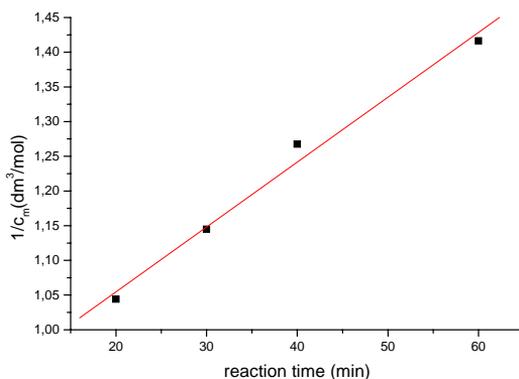
Figure 8

The change in the inverse of the momentary monomer concentration reaction with increasing reaction time at temperature 313 K

The equation for the change of rate in time at temperature 313 K:

$$Y= 0{,}86759\ (\pm\ 2{,}963\cdot10^{-2}) + 0{,}00935\ (\pm\ 7{,}34973\cdot10^{-4})\ X \qquad\qquad R = 0{,}99388$$
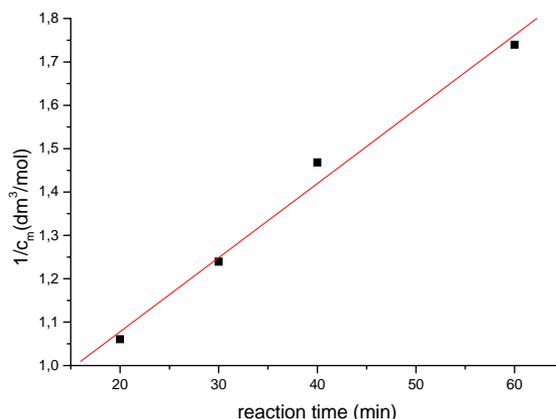
Figure 9

The change in the inverse of the momentary monomer concentration reaction with increasing reaction time at temperature 323 K

The equation for the change of rate in time at temperature 323 K:

$Y = 0{,}73603\ (\pm\ 5{,}478 \cdot 10^{-2}) + 0{,}01709\ (\pm\ 1{,}360 \cdot 10^{-3})\ X$ $R = 0{,}99374$

Conslusions

On the basis of my investigations I have stated that the grafting of industrial cellulose fibre with vinyl-acetate monomer, cerium(IV)-ammonium-sulphate initiator can be carried out. When studying the kinetics of the process I have stated that the gross reaction of grafting industrial cellulose with vinyl-acetate monomer is a second order reaction, which is proven by the fact that the invert of the momentary monomer concentration of the system plotted against time is a linear function. The reaction rate increases when the temperature in the range of 293-323 K is increasing, while the average activation energy decreases.

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