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Torque measurement as a tool to monitor the breakdown of cassava starch gels, by the effect of Fenton's initiator for graft copolymerization

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ABSTRACT

The use of a combined stirrer-torque meter allows for monitoring viscosity during polymerizations and other reactions, much faster and more continuous than off-line viscosity measurements. This method was applied in previous research about the grafting of acrylic acid onto cassava starch using Fenton's initiator. In this article the method is used to assess the effect of Fenton's initiator on gels of cassava starch in the absence of the monomer. The intention here is to activate the starch selectively first, which could improve graft selectivity. The interaction of a redox graft copolymerization initiator with starch gels when there is no monomer in the system yet, is hardly ever addressed in grafting literature. Remarkably, the present experimental study shows a rapid viscosity decrease of the starch gel, in the order of 70% in less than 2 min, at conditions reflecting graft copolymerization. This result must be considered a major setback for the application of pre-initiation. Torque measurement also allows to identify the important steps in the reaction of Fenton's reagent with starch without the need to do other, more intensive analyses on the chemistry. For example, it could be concluded that the second stage of Fenton's reaction, the slower decomposition of hydrogen peroxide by Fe^{3+} ions, accounts for another 20% loss of the original gel viscosity but over a longer period, some 30–60 min. Possible further decrease over a longer period is too slow or small relative to the measuring accuracy of the torque meter. FTIR analyses show the occurrence of peaks at 1730–1740 cm^{-1} in starch which has been subjected to reaction with Fenton's. These peaks are in the range of the vibrational frequencies associated to C=O bonds, that are not present in the original starch. This provides at least a strong indication for oxidative degradation of the starch chains.

Introduction

Graft copolymerization of acrylic monomers onto starch is a well investigated method to synthesize alternatives for current performance polymers from petrochemical feedstocks. Using the biopolymer starch, these products have the aspects of renewability and biodegradability that would fit into a circular economy [1]. The problems associated with non-degradable plastics were recently highlighted again by Castelvetro et al. [2]. Meimoun et al. [3] published a review that gives a good overview of the many combinations of starch, monomers and initiators that have been investigated for graft polymerizations. Fanta and Doane [4] also present a lot of details on the various initiation methods and starch-monomer-solvent systems that have been reported in articles and patents. In the research project at Groningen University, graft copolymerization of acrylic acid onto gelatinized cassava starch in water

solvent has been investigated, using Fenton's reagent as an initiator [1,5,6]. With this water-soluble monomer, there is a homogenous system that has the advantage of a simple and direct process. However, with a non-selective initiator and all of the reactants in the same aqueous phase, the formation of homopolymer is all but inevitable. In previous work it was found that the rate of homopolymerization dominates over the graft reaction, also at conditions that gave an optimum in the grafting yield [5]. Several options are available to cope with the issue of homopolymer formation. For example, when a crosslinker is applied, the overall selectivity for grafted polyacrylic acid (PAA) is better [1,6]. Alternatively, to prevent the necessity of an uneconomic separation, the result of the graft reaction including the homopolymer can be also considered as a final product [1,7].

Another option that may have great beneficial effect on the graft selectivity is pre-initiation, activating starch into a macroradical before

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Table 1

Viscosity decrease by the exposure of gelatinized potato starch to three initiation systems.

Initiation system	Viscosity decrease after	
	20 min	40 min
K ₂ S ₂ O ₈	84%	84%
Ascorbic acid/H ₂ O ₂	32%	40%
Fe ²⁺ /H ₂ O ₂	64%	68%

Conditions: 40 °C, 5% wt/wt gelatinized potato starch in water, initiator radicals to AGU always at 1:40 M ratio.

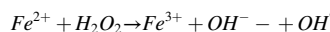
entering monomer. Interesting papers in this respect were published by Reyes et al. [8] and by Fanta and Doane [4]. And more recently, pre-activation was also applied successfully by Ishihara et al. for graft copolymerizations onto various polymer substrates [10]. After pre-initiation of starch by irradiation, almost 100% selectivity for the graft reaction was reported, with acrylic acid in water. However, in the work of Reyes et al. and Ishihara et al. [8–10], the creation of radicals in starch was done by high energy radiation which is subject to severe drawbacks when industrial application is considered [9]. In several more recent articles, creation of radicals onto starch by chemical reaction before contacting the activated starch or cellulose to monomer was also reported [11–15]. A positive influence on the grafting results was always claimed, but in none of these papers the possibility neither the observation of damage to the carbohydrate backbone chains was mentioned. Still, some degradation of starch must be expected when its molecules are being exposed to oxidizing agents like ammonium persulfate [13,14]. It is quite possible that some starch breakdown is compensated by the build-up of a polymer structure by the grafting reaction. Desmet et al. [11] report on degradation of cellulose chains when exposed to γ -radiation before monomer was added. Perhaps some degradation of starch backbones is not really a problem, as several authors, e.g. Mostafa et al. [16], Berndl [17] and more recently Djordjevic et al. [18] have demonstrated that relatively short chains of carbohydrates can be graft modified into functional copolymers for several applications.

Considering the application of pre-initiation, a time span of perhaps a few minutes may be needed between the addition of initiator components and monomer, to allow for good mixing first. During this period, starch macroradicals must be created that should sustain activity while not affecting the integrity of the backbone too much. In virtually dry starch, radicals can live for many hours or even days [4,19]. In an aqueous environment, radical lifetime is uncertain but at least much shorter. To explore the feasibility of pre-initiation with Fenton's, some test reactions were done. After the addition of both initiator components at a 2 min interval (Fe²⁺ and H₂O₂), the monomer was added after 5 min. The results were really disappointing. After the experiment a clear fluid was obtained with no sign of any substantial polymer formation, while

viscosity was much lower compared to the initial gelatinized starch solution. Apparently, the starch chains had been degraded and the radicals de-activated before they could react with monomer. Such an effect of Fenton's oxidator on starch, hydrolyzing and degrading chains to a lower viscosity, was already reported in 1936 by Brown [20]. It is therefore perhaps surprising that an effect of initiation agents, either Fenton's or any other redox system, on starch backbones is almost never addressed in the vast literature on starch grafting. Two of the exceptions are articles published by Fanta et al. [21] and by Hsu et al. [22]. In the work of Fanta, it is clearly demonstrated that three common graft polymerization initiation systems, Co⁶⁰ irradiation, Ceric Ammonium Nitrate (CAN) and Fenton's reagent, have a pronounced and detrimental effect on the integrity of wheat starch. Also, oxidative degradation of starch chains was confirmed by the presence of acetal groups in the treated starches [21]. In Hsu et al. [22], degradation of the marine polysaccharide chitosan by ammonium persulfate, which is also a much used graft polymerization initiator, is investigated. These authors use off-line viscosity measurement and also apply mol weight determinations to samples taken at certain time intervals over a period of one hour. At every interval, there is both lower viscosity and lower average mol weight, which is a clear indication of degradation of the chitosan. To see rapid changes however, continuous measurement would be more suitable. The article of Ogiwara and Kubota also addresses the scission of backbone chains by Fenton's components during graft copolymerization, but with cellulose [23].

In the laboratory in Groningen, another exploratory study was carried out to test the effect of three possible initiators (Fenton's, Potassium Persulfate and Ascorbic acid/H₂O₂) on the viscosity of gelatinized potato starch was investigated. These results are shown in Table 1. In these experiments, the use of NaOH to assist the gelatinization of potato starch may also have caused some chain degradation. Also, the high stirring speed applied in those early experiments (700 rpm) may enhance the contribution of starch viscosity decrease by thixotropic effects [24,25], a physical effect. Despite that, the conclusion from the results from Table 1 is similar to the findings of Fanta et al. [21] with wheat starch and Hsu et al. [22] with chitosan. In Table 1, a substantial decrease of the viscosity of the gelatinized starch is observed with all of the initiation systems tested. The ascorbic acid system has the most moderate effect on starch viscosity but was also found to be less effective in the initiation of graft copolymerization.

In previous work, torque measurement was successfully applied to monitor the viscosity of a gel during the graft copolymerization of acrylic acid onto cassava starch [24], which was recognized as a step forward in experimental monitoring of reactions [25]. In the present paper, an experimental study is reported applying this torque measurement method also as a tool to explore the effect of Fenton's initiator on the integrity of cassava starch gel. In order to obtain the effect of the initiator only, no monomer was added during these experiments. Conditions were chosen such as to further resemble the grafting reaction. The effect of variations of the process parameters was taken into account: the concentration of gelatinized starch in water, the Fe²⁺/AGU ratio, the ratio of Fe²⁺ to H₂O₂ and also whether Fe³⁺ is active in creating radicals from hydrogen peroxide that could be capable of degrading starch. To test whether a viscosity decrease was caused by oxidative degradation of the starch molecules, infrared spectroscopy (FTIR) was applied on selected samples. The reaction formula by which the Fenton's reaction produces the initial radicals is shown below (Eq. (1)).



When there is excess H₂O₂, as usual in the application of Fenton's reagent, further reactions of the produced Fe³⁺ with the remaining hydrogen peroxide are possible. In Fig. 8 an overview is presented including further reactions, a scheme that is also based on the results presented in this paper.

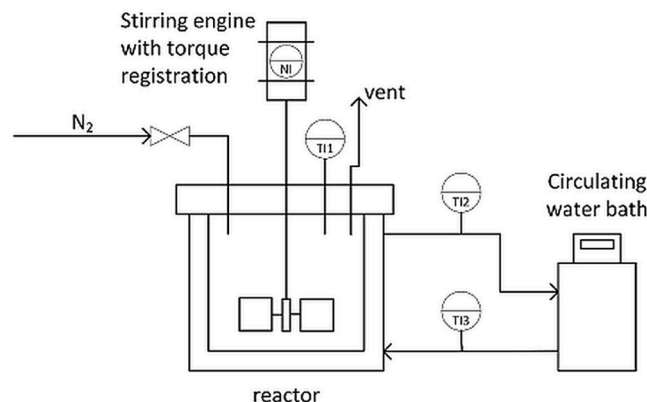


Fig. 1. Scheme of the batch reactor and the stirrer-torque meter.

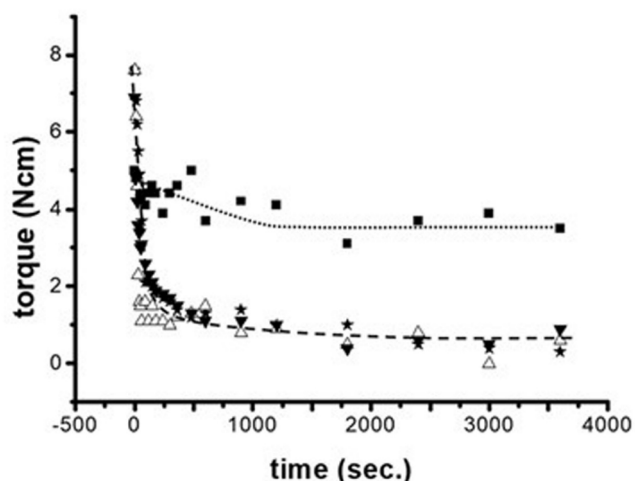


Fig. 2. Three runs at the 'reference conditions' ($\Delta^{\ast}\blacktriangledown$) compared to torque decrease by starch thixotropy (\blacksquare).

Experimental

Materials

The native cassava starch used in this study was provided by AVEBE-Indonesia. FAS (Ferrous Ammonium Sulfate), H_2O_2 (Hydrogen Peroxide) 30% were reagent grade chemicals and were used as received after purchase from Sigma-Aldrich company.

Equipment and reaction procedure

Starch reactions with Fenton's were performed in a stainless steel batch reactor of 500 ml content, fitted with a water jacket to control reaction temperature. The set up was equipped with a Heidolph RZR 2102 control combined stirrer-torque meter as reported in previous work [1,24]. Fig. 1 shows the experimental set up. Cassava starch and highly purified (milliQ) water were entered in the reactor. Starch was gelatinized at 70 °C for 25 min and after that, the reactor content was cooled to reaction temperature before being subjected to the effect of the initiator. These experiments were carried out at 40 °C, the temperature selected for comparable graft copolymerizations [1,4]. The initiator components Ferrous Ammonium Sulfate (FAS) and H_2O_2 were added at a two minutes interval. Time counting was started at the moment the peroxide was added. Initiator concentration for a reference experiment, designated here as 'standard conditions', was chosen such as to have 1 mol of Fe^{2+} per 100 AGU-groups and a 10:1 M surplus of H_2O_2 over the ferrous ions. Practically, for the run with 12% (w/w) starch this means $7.45 \times 10^{-3} \text{ mol/l}$ of Fe^{2+} (FAS) and $74.5 \times 10^{-3} \text{ mol/l}$ H_2O_2 .

FTIR-spectroscopy

If starch has been oxidized, a part of the original OH-groups are turned into acetal (C=O) groups [22,26]. In an infrared spectrum such C=O groups may be detected as a peak at ca 1780 cm^{-1} . Therefore, Fourier Transformation Infra-Red (FTIR) analysis was performed using a Spectrum 2000 FT-IR Spectrometer (Perkin Elmer, Norwalk, CT, USA) in the range $4000\text{--}400 \text{ cm}^{-1}$.

Results and discussion

Starch concentration

In most graft copolymerization reactions at the laboratory [1], the concentration of gelatinized starch had to be limited to 7.5% since the

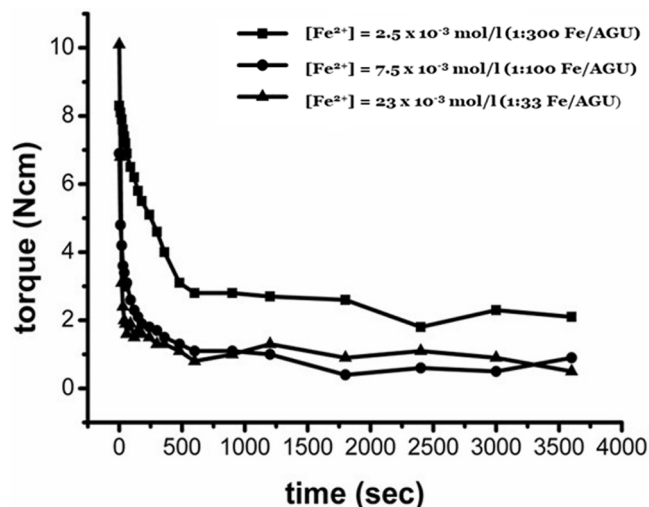


Fig. 3. Effect of the Fe^{2+} /AGU ratio.

growth of grafted chains causes a large increase of the viscosity of the reaction mixture [24]. Since in the experiments reported in the present paper, there is no grafting and only a descent of the torque/viscosity, runs could be started with a higher starch concentration. It was found that 12 wt% gelatinized starch gives a better signal to noise ratio and therefore more accurate readings from the torque meter [1]. A higher concentration was also tested, but at 15% gelatinized starch, gel homogeneity could not be made certain. Consequently, all runs reported below were performed with 12 wt% gelatinized starch.

Reproducibility of the 'reference experiment' and comparison to thixotropic effects

A set of conditions was chosen as a reference, to make parameter variations around. Besides the choice for 12% starch load, conditions were chosen to resemble the runs with graft polymerizations as mentioned in section 2.2: molar ratios of Fe^{2+} to AGU of 1:100 and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ 10:1, and reactions at 40 °C and 300 rpm stirring speed. Three runs were made at these conditions, to test the reproducibility of the torque measurements. The results are shown in Fig. 2. The measured points of these three runs at the same conditions show only minute differences. These differences are really small as compared to those observed in all other graphs. So this triplicate experiment gives the confidence that the trends and differences shown in the other graphs can be considered significant. To test whether starch thixotropy does not cause the observed decrease when Fenton's is used, a run with just stirring of the gelatinized starch was made and also depicted in Fig. 2. It is clear that the effect of starch thixotropy by mechanical stress is much lower than the decrease in the apparent viscosity caused by the reaction with the initiator.

Effect of the initiator concentration on viscosity decrease

Variation of the initiator concentration, the ratio of Fe^{2+} to AGU, was tested. In all cases, the molar ratio of H_2O_2 to FAS was maintained at 10:1, and other conditions are equal to the reference experiment. The results in Fig. 3 show that starch breakdown at the molar ratio of Fe^{2+} /AGU of 100 is already so rapid that a threefold increase of the amount of initiator makes it only gradually faster. But, at the lowest initiator dosage it takes longer before torque reaches almost steady state. Perhaps, some thixotropy may be a factor at that stage. Also, the steady level is higher, corresponding to less degradation of the original starch molecules. The observation that the dosage of initiator is an important factor in the degree of chain degradation could be expected, and is also

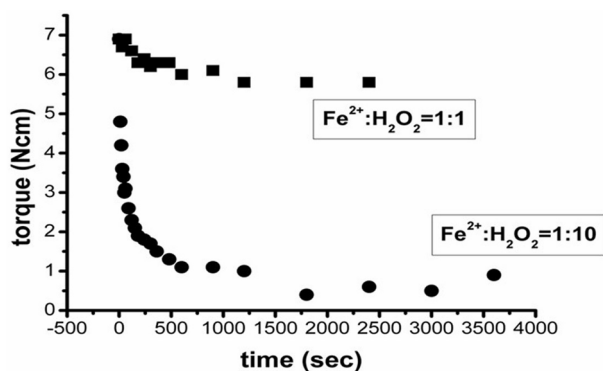


Fig. 4. Torque decrease at different molar ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$.

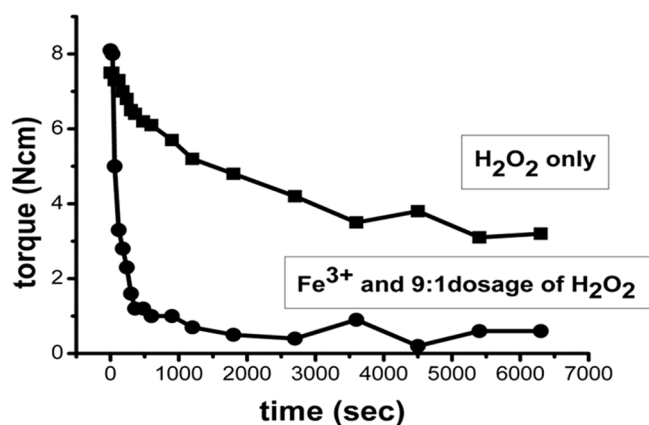


Fig. 5. Comparison of pure H_2O_2 with the effect of Ferric iron added.

consistent with results of Desmet et al. [11] with cellulose.

Effect of the ratio of H_2O_2 to Fe^{2+}

In previous work [1,5] it was concluded that a 10:1 excess of hydrogen peroxide to FAS (Fe^{2+}) was preferable over an equimolar dosage, to be certain to produce sufficient amounts of radicals to initiate the graft copolymerization. In the foregoing it was shown that the effect of the oxidative power of the initiator on gelatinized starch viscosity is very pronounced. This provides the opportunity to investigate the effect of the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio in some more detail also with the method or torque measurement. In these experiments, the ratio of Fe^{2+} to AGU is kept constant at 1:100 while the dosage of hydrogen peroxide has been varied. In Fig. 4 the result of a run at $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1:1$ (mole/mole) is shown. There is surprisingly little viscosity decrease which mostly occurs in the first 5–10 min after the addition of the initiator components. Logically, the production of radicals does not continue when the reaction of Fe^{2+} with the available stoichiometric amount of peroxide has worked out. The slight further decrease after the first minutes is in the order of changes caused by thixotropic behavior of gelatinized starch. The oxidation of Fe^{2+} proceeds very fast, as known from literature [27,28] which was also seen in a simple separate experiment. When hydrogen peroxide is added to a beaker with a FAS-solution, the color change from green to reddish-brown takes place almost instantaneously, even without intensive mixing. It can be concluded that when the components of Fenton's reagent are joined, there is almost an explosion of radicals. These radicals can cause fast breakdown of the starch chains. But also, such an abundance of radicals must lead to relative many auto-terminations, which would explain why starch breakdown rapidly stops at the 1:1 $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio.

By the comparison of the data in Fig. 4 it is clear that at much higher

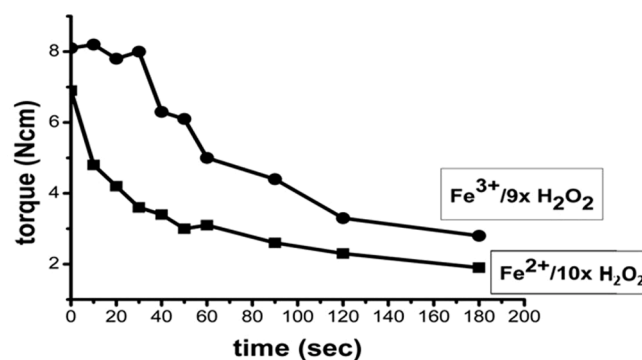


Fig. 6. Viscosity decrease with Fe^{2+} versus with only Fe^{3+} , with similar amounts of hydrogen peroxide added.

H_2O_2 dosage starch chain breakdown and viscosity decrease continue, where at the 1:1 ratio it almost stops after just a few minutes. But, sustained starch degradation can only occur when new radicals are being produced from follow-up reactions, after the initial amount of Fe^{2+} has been consumed. There are several possible mechanisms for the creation of fresh radicals from the 90% of the H_2O_2 which has not reacted yet. Most logical would be either auto-dissociation of H_2O_2 , or the formation of radicals from the reaction of the ferric ions that were formed in the first step. Calculations made from literature information [29,30] however show that auto-dissociation is probably very slow at this temperature (40 °C) while dissociation of hydrogen peroxide by trace elements is unlikely since commercial hydrogen peroxide with a stabilizer was used in these experiments.

The auto-dissociation option was tested by the experiments shown in Fig. 5. One experiment was done with only H_2O_2 in a dosage equal to the reference experiment, 7.45×10^{-2} mol/L. Here torque decrease is slow and comparable to the influence of starch gel thixotropy. In the second experiment, 90% of the original hydrogen peroxide (9:1 $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ molar ratio) was added to resemble the condition in the system after the first reaction step, the oxidation of the Fe^{2+} . In the second experiment, viscosity decline is much faster. Therefore, it can be concluded that the ongoing starch degradation is mainly caused by radicals created from reactions of Fe^{3+} with H_2O_2 . However, the rate of decrease of the starch gel viscosity when only Fe^{3+} was added is still lower than with Fe^{2+} , especially in the first few minutes as can be seen in Fig. 6. The difference in viscosity decrease is most pronounced in the first ca 60 s after addition of the different grades of iron. After the first few minutes, the viscosity reduction by the influence of Fe^{2+} versus Fe^{3+} is not very different, which is logical since at this stage the original ferrous ions must have been consumed. These findings are consistent with results from Brown [20]. For a more precise discrimination between the reaction rates of the various iron species, starch degradation may not be the best tracer reaction since relatively few chain scissions can already cause a large effect on the overall viscosity of the fluid.

Separate initiator reactions in a glass beaker show that every new addition of H_2O_2 results in new formation of oxygen bubbles; long after the original amount of Fe^{2+} was oxidized. An experiment with addition of H_2O_2 after a reaction similar to the run shown in Fig. 4 (equal molar amount of Fe^{2+} and H_2O_2 to start with) also appeared to give additional viscosity decrease. Such results point to the conclusion that Fe^{3+} creates radicals from fresh hydrogen peroxide molecules, which is known from literature [27,28,31]. In the present work however, it is observed that these radicals are sufficiently active to degrade starch molecule, probably by the mechanism discussed below.

A larger but still compact scheme for reactions of Fenton's reagent

In several articles on starch graft copolymerization or other reactions with Fenton's, only the reaction of Fe^{2+} with H_2O_2 is mentioned as

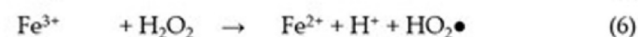
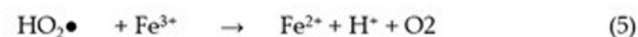
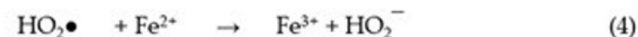
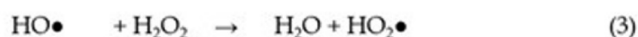


Fig. 7. Extended reaction scheme of Fenton's initiation system excluding further reactions with starch and/or monomer.

source of radicals [32–35]. This has also been assumed in previous work [5]. However, from the present results, it is clear that such is a too rigorous simplification which may only be relevant when no excess hydrogen peroxide is applied. Also in literature there is ample evidence for reactions involving Fe^{3+} , e.g. in the review of Uri [31] and in the research of Vasquez et al. [32]. From such sources, many detailed radical reaction steps can be obtained. A selection was made from these, to obtain the reaction steps that can be regarded relevant to explain the phenomena observed in the experiments reported in the foregoing. This scheme is shown in Fig. 7.

Baxendale et al. [27] stated that reaction (2) is suppressed in the presence of sufficient amounts of monomer ethylene, which at least would simplify the kinetic analysis of polymerizations. With monomer already in the system, it is likely that there will not be much starch degradation since most of the radicals will initiate the polymerization reactions instead. The combination of (reaction steps (3) and (5) constitutes a catalytic cycle for the iron species. Such a cycle would explain that in several sources like in the patent of Masuda [36] it was mentioned that traces of iron can be sufficient to start or enhance polymerization reactions when there is H_2O_2 in the system.

Still, the $\text{HO}_2\bullet$ radical has a lower reactivity to substrates like starch and monomer [27,31]. It may even be questionable whether the oxidizing power of the hydroperoxyl radical is able to react with starch-hydroxy groups since it shows low activity in oxidizing primary alcohols [37]. Also, this radical could be terminated via reaction (4). Reaction (6) in Fig. 7 is the step that can explain the creation of radicals when only Fe^{3+} and H_2O_2 are started with, like observed in Figs. 5 and 6. By this

reaction the less active radical $\text{HO}_2\bullet$ would be formed, which fits in the observations of lower reaction rate in starch degradation seen in Fig. 6. But, this reaction also produces new Fe^{2+} that will show the same very fast reaction with available H_2O_2 molecules into the highly active $\text{OH}\bullet$. It is therefore likely that the combination of steps (5) and (6) determines the rate of further starch degradation. The occurrence of reactions that produce H^+ was confirmed by the measured distinct decrease in pH values. It can be concluded that the extended but still compact scheme of Fig. 7 is sufficiently detailed to explain the experimental findings reported in this exploratory study. They also confer to the findings of Ogiwara and Kubota [22].

Proof of the oxidation of starch by the initiator

When an $\text{OH}\bullet$ radical reacts with starch, the most likely reaction is the abstraction of an H-atom from one of the hydroxyl groups, creating a radical at the starch backbone. When this radical reacts with another $\text{OH}\bullet$, it results in the formation of a C=O acetal group. Also, upon starch oxidation a part of the glucoside linkages between AGU groups is broken and the starch molecules are divided into smaller fragments [24]. The end groups are also C=O, acetals. This means that if C=O bonds could be detected in the starch that was exposed to initiator, it would prove that oxidative degradation of starch must have occurred. For this purpose, FTIR spectra were made and shown in Fig. 8.

In an IR spectrum, C=O bonds can show up in the range between 1800 and 1600 cm^{-1} depending on the surrounding structures. In acetone with two methyl groups at the sides, the C=O stretch vibrations are found in the range 1720–1705 cm^{-1} . It can be expected that when several more electronegative oxygen atoms are in close, the peak associated to a C=O bond shifts to somewhat higher frequencies since the bond becomes shorter, has a higher bonding strength so that more energy is required to activate stretch vibrations. In Fig. 8 it is seen that in native starch (highest line) there is no peak that can be associated to C=O stretch vibrations. A tiny peak was observed in the starch after exposure to 1:100 Fe^{2+} to AGU. To validate whether this is likely to be a C=O peak, a portion of starch was also subjected to heavy oxidative treatment. With 1:5 Fe^{2+} /AGU and 10:1 H_2O_2 / Fe^{2+} there are, in theory, two $\text{OH}\bullet$ radicals per AGU. In this severely oxidized starch the peak at 1734 cm^{-1} is much larger, in the lower line in Fig. 8. The actual position of the lines is less relevant than the ratio between the various peaks at about this frequency, which can shift a bit dependent on neighboring structures. These results confirm that oxidative degradation has

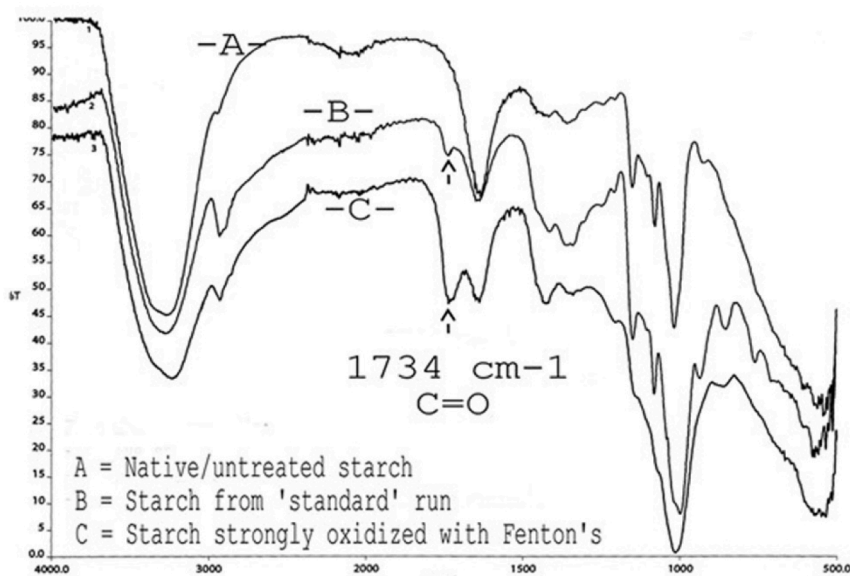


Fig. 8. FTIR spectra of starches at increasing degree of oxidation.

occurred also at the lower exposure level of cassava starch to Fenton's reagent. It is the most likely reason for the viscosity decrease observed in the experiments.

Conclusions

The torque measurements reported in this study show that severe viscosity decrease occurs when starch is exposed to Fenton's reagent in the absence of monomer. This is an effect that can be expected when an initiator with oxidative power is contacted to starch when there is no monomer there yet, but is hardly ever addressed in literature on starch grafting. These degradation studies provide for an explanation why previous experiments to try to initiate starch before adding monomer have failed to give graft copolymerization. Therefore, this pathway to improve the selectivity of the grafting versus the homopolymerization reaction seems not feasible, at least not with the Fenton's initiation system. When there is monomer already in the system, there is not much chance for starch to be degraded since many more reactive molecules are present to catch the primary radicals.

Although torque registration is not extremely precise, so far it has been a useful tool to observe the change of viscosity during polymerization reactions. The present experimental studies also provide for an improved insight into the mechanism of Fenton's reagent, especially towards the production of radicals that can degrade starch. It is clear that considering only the initial reaction of Fe^{2+} with H_2O_2 as the sole radical production mechanism is too much of a simplification. Radical production continues long after the added amount of Fe^{2+} has been oxidized. It is proven by dedicated experiments that this continued radical production involves reactions with Fe^{3+} , thereby confirming literature data related to this topic. The major part of the starch breakdown has even occurred during this period of continuing radical formation. An expanded scheme could be made up from literature information, a scheme that is still not too complex but provides for a good explanation of the effects that have been observed in this experimental study. Additionally, FTIR spectra confirm the formation of $\text{C}=\text{O}$ groups corresponding to oxidative degradation of starch.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Witono, J.R. *New materials by grafting of acrylic acid onto cassava starch*, in *Chemical Engineering Dept.* 2012. University of Groningen: The Netherlands.
- Biale, G., La Nasa, J., Mattonai, M., Corti, A., Vinciguerra, V., Castelvetto, V., Modugno, F. *A Systematic Study on the Degradation Products Generated from Artificially Aged Microplastics*. *Polymers*. 13(12). 2021. DOI: 10.3390/polym13121997.
- J. Meimoun, V. Wiatz, R. Saint-Loup, J. Julien Parcq, A. Audrey Favrelle, F. Bonnet, P. Zinck, *Modification of starch by graft copolymerization*, *Starch/Stärke* 70 (2018).
- Fanta, G.F., Doane, W.M., *Grafted Starches*. In *Modified Starches: Properties and Uses*, O.B. Wurzburg, Editor. 1986. CRC Press.
- J.R. Witono, I.W. Noordergraaf, H.J. Heeres, L.P.B.M. Janssen, *Graft Copolymerization of Acrylic Acid to Cassava Starch—Evaluation of the Influences of Process Parameters by an Experimental Design Method*, *Carbohydrate Polymers* 90 (4) (2012) 1522–1529.
- J.R. Witono, I.W. Noordergraaf, H.J. Heeres, L.P.B.M. Janssen, *Water Absorption, Retention and the Swelling Characteristics of Cassava Starch Grafted with Polyacrylic Acid Carbohydrate*, *Polymer* 103 (2014) 325–332.
- I.-W. Noordergraaf, T. Fourie, P. Raffa, *Free-Radical Graft Polymerization onto Starch as a Tool to Tune Properties in Relation to Potential Applications, A Review*. *Processes* 6 (4) (2018) 31, <https://doi.org/10.3390/pr6040031>.
- Z. Reyes, M.G. Syz, M.L. Huggins, C.R. Russell, *Grafting acrylic acid to starch by preirradiation*, *Journal of Polymer Science Part C: Polymer Symposia* 23 (1) (1968) 401–408.
- Z. Reyes, C.F. Clark, M. Comas, C.R. Russell, C.E. Rist, *Continuous Production of Graft Copolymers of Starch with Acrylamide and Acrylic Acid by Electron Preirradiation*, *Nuclear Applications* 6 (5) (1969) 509–517.
- R. Ishihara, S. Asai, K. Saito, *Recent Progress in Charged Polymer Chains Grafted by Radiation-Induced Graft Polymerization*, *Quantum Beam Sci.* 4 (2) (2020) 20, <https://doi.org/10.3390/qubs4020020>.
- G. Desmet, E. Takács, L. Wojnárovits, J. Borsá, *Cellulose functionalization via high-energy irradiation-initiated grafting of glycidyl methacrylate and cyclodextrin immobilization*, *Radiation Physics and Chemistry* 80 (12) (2011) 1358–1362.
- P.C. Parvathy, A.N. Jyothi, *Water sorption kinetics of superabsorbent hydrogels of saponified cassava starch-graft-poly(acrylamide)*, *Starch – Stärke* 64 (10) (2012) 803–812.
- M.D. Teli, N.G. Waghmare, *Synthesis of superabsorbent from carbohydrate waste*, *Carbohydrate Polymers* 78 (3) (2009) 492–496.
- Q. Zhang, K. Xu, P. Wang, *Study on structure and molecular dynamics of starch/poly(sodium acrylate)-grafted superabsorbent by ^{13}C solid state NMR*, *Fibers and Polymers* 9 (3) (2008) 271–275.
- Zhu, S., Jiang, L., Zhang, H. *Synthesis of Cationic High Polymeric Flocculants from Starch-Graft-Poly (DMAAC-co-AM) and Application in Fine Coal Slurry Progress in Environmental Science and Technology* 2009. 2. 1290-1295.
- K.M. Mostafa, A.A. El-Sanabary, *Synthesis and Characterization of Novel Smart Flocculant Based on Poly(MAam)-Pregelged Starch Graft Copolymers and Their Degraded Products*, *Advances in Polymer Technology* 32 (2) (2013) n/a–n/a.
- G. Berndl, *Untersuchungen an polymeren Wachmitteladditiven auf Basis von Propfocopolymeren ungesättigter Carbonsäuren auf Stärkeprodukte*, University of Regensburg, Germany, 1995.
- S. Djordjevic, L. Nikolic, S. Kovacevic, M. Miljkovic, D. Djordjevic, *Graft copolymerization of acrylic acid onto hydrolyzed potato starch using various initiators*, *Periodica Polytechnica Chemical Engineering* 57 (1–2) (2013) 55–61.
- C.C. Lee, C.H. Chen, *A Note on the Disappearance of Radicals Trapped in Gamma-irradiated Starch and Gluten*, *Cereal Chemistry* 42 (1965) 573–576.
- W.R. Brown, *The Hydrolysis of Starch by Hydrogen Peroxide and Ferrous Sulfate*, *The Journal of Biological Chemistry* 113 (1936) 417–425.
- G.F. Fanta, R.C. Burr, C.R. Russell, C.E. Rist, *Modification of Wheat Starch by Initiation Systems Used for Graft Polymerization*, *Cereal Chemistry* 47 (1970) 85–91.
- S.-C. Hsu, T.-M. Don, W.-Y. Chiu, *Free Radical Degradation of Chitosan with Potassium Persulfate*, *Polymer Degradation and Stability* 75 (1) (2002) 73–83.
- Y. Ogiwara, H. Kubota, *Comparison of the Fe^{2+} - H_2O_2 and Fe^{3+} - H_2O_2 Initiation Systems in Graft Copolymerization of Cellulosic Materials*, *J. App. Polym. Sci* 13 (1969) p1613–p1620.
- J.R. Witono, I.W. Noordergraaf, H.J. Heeres, L.P.B.M. Janssen, *Rheological Behavior of Reaction Mixtures during the Graft Copolymerization of Cassava Starch with Acrylic Acid*, *Polymer Engineering and Science* 57 (12) (2017) 1285–1292.
- Witono, J.R., Noordergraaf, I.W., Heeres, H.J., Janssen, L.P.B.M. *Rheological Behavior of Reaction Mixtures during Graft Copolymerization*. *Advances in Engineering*, May 4, 2018.
- Whistler, R.L., Bemiller, J.N., Paschall, E.P. (eds). *Starch, Chemistry and Technology*, ed. 2nd. 1984: Academic Press, Inc.
- J.H. Baxendale, M.G. Evans, C.S. Park, *The mechanism and kinetics of the initiation of polymerisation by systems containing hydrogen peroxide*, *Transactions of the Faraday Society* 42 (1946) 155–169.
- C. Walling, *Fenton's Reagent Revisited*, *Accounts of Chemical Research* 8 (4) (1975) 125–131.
- J. McKenzie, *Hydrogen Peroxide without Accidents*, *Chemical Engineering* June (1990) 84–90.
- J. Takagi, K. Ishigure, *Thermal Decomposition of Hydrogen Peroxide and the Effect on Reaction Water Monitoring of Boiling Water Reactors*, *Nuclear Science and Engineering* 89 (1985) 117–186.
- N. Uri, *Inorganic Free Radicals in Solution*, *Chem Rev* 50 (1952) 375.
- B. Vázquez, I. Goñi, M. Gurruchaga, M. Valero, G.M. Guzmán, *A Study of the Graft Copolymerization of Methacrylic Acid onto Starch Using the $\text{H}_2\text{O}_2/\text{Fe}^{++}$ Redox System*, *Journal of Polymer Science: Part A: Polymer Chemistry* 27 (2) (1989) 595–603.
- S. Hashemian, *Fenton-Like Oxidation of Malachite Green Solutions: Kinetic and Thermodynamic Study*, *Journal of Chemistry* 2013 (2013) 7.
- L.C. Ong, Y.H. Lin, T.H. Wang, *Measuring Fenton's reaction kinetics at one-second intervals* *Journal of Environmental Science and Health, Part A* 36 (7) (2001) 1427–1435.
- S. Wang, *A Comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater, Dyes and Pigments* 76 (3) (2008) 714–720.
- Masuda, F., Nishida, K., Nakamura, A. *Water Absorbing Starch Resins*, in *US Patent*, 4076663, Editor. 1978. Sanyo Chemical Industries, Ltd.
- Green, J.W. In *The Carbohydrates: Chemistry and Biochemistry* (Volume I Part B), W. Pigman, Editor. 1980. Academic Press Inc. 1131.