Paper chemistry

Jenna Raunio*, Ekaterina Nikolskaya and Yrjö Hiltunen

On-line monitoring of cationic starch gelatinization and retrogradation by ^1H NMR-relaxometry

<https://doi.org/10.1515/npprj-2018-0010>

Received June 6, 2018; accepted July 11, 2018; previously published online August 23, 2018

Abstract: The gelatinization of cationic starch during a heating-holding-cooling cycle in a batch cook was monitored by measuring ^1H NMR spin-spin relaxation rates R_2 on-line. The effect of storage time and temperature (8, 20 and 60 °C) on cationic starch retrogradation was also studied. Clear differences were measured between the gelatinization and retrogradation behavior of potato starch and cereal starches (wheat and barley). The potato starch gelatinized completely when cooked at 95 °C at normal pressure, whereas cereal starches gelatinized only partially. Partial gelatinization lead to rapid retrogradation upon cooling. For fully gelatinized starch, the beginning of retrogradation was slower and began at a lower temperature. NaCl and Na_2SO_4 did not have a significant impact on the gelatinization of wheat starch but did affect retrogradation. The results show that NMR-relaxometry is suitable for following starch gelatinization on-line from a batch cook and that it can be used to determine whether gelatinization is complete. This technique can thus be a useful tool in paper mills for the on-line quality control of starch solutions.

Keywords: batch cook; cationic starch; gelatinization; ^1H NMR-relaxometry; on-line measurement; paper chemicals; retrogradation.

Introduction

Cationic starch is an essential additive in papermaking for improving the retention, strength, dewatering and formation of the product (BeMiller 2005, Stenius 2007). To make high-quality paper, starch must be properly gelatinized before it can be added to the paper machine, because only then can it properly bond with cellulose fibers (Neimo 1999). The gelatinization, i. e., cooking, can occur in a *jet-cooker* at elevated pressure at 120–160 °C, which is the most common method used in paper mills, or in a batch cooker at normal pressure at 90–95 °C (Lehtinen 2000), which is the method used in this study. At the molecular level, gelatinization begins with water diffusing into the amorphous part of the starch granules, which causes the granules to swell (Ritota et al. 2008). After this effect, the crystalline portions of the granules begin to disintegrate as the double and single helices of amylopectin and amylose begin to unwind and hydrogen bonds begin to break (Wang et al. 2015). In addition to a high temperature, shear forces are also needed to disintegrate the remaining granules completely (Hermansson and Svegmärk 1996).

If the granules do not dissolve completely, i. e., the cook is incomplete, loosely connected particles made of amylopectin, sometimes called *ghost particles*, can remain in the solution (Smits et al. 2003). Such particles can be detrimental for papermaking processes, which is why jet cooking is a good technique for starch cooking in paper mills (Hermansson and Svegmärk 1996). Electrolytes present in the cooking solution can either prevent granules from melting (NaCl and Na_2SO_4) or facilitate melting (hydroxides such as NaOH or KOH). Due to this effect on granule melting, these salts either increase or decrease the required cooking temperature (Maurer 2007).

Retrogradation occurs when amylose and amylopectin begin to reorganize as the gelatinized solution cools (BeMiller 2005). Amylose begins to form single helices, and the side-branches of amylopectin begin to form double helices. As the process advances, amylose forms a network in the solution, which binds together crystallites

*Corresponding author: Jenna Raunio, FiberLaboratory, South-Eastern Finland University of Applied Sciences, Vipusenkatu 10, 57200, Savonlinna, Finland, e-mail: jenna.raunio@xamk.fi, ORCID: <http://orcid.org/0000-0003-3565-4656>

Ekaterina Nikolskaya, Yrjö Hiltunen, FiberLaboratory, South-Eastern Finland University of Applied Sciences, Vipusenkatu 10, 57200, Savonlinna, Finland, e-mails: ekaterina.nikolskaya@xamk.fi, yrjo.hiltunen@xamk.fi

formed by amylopectin (Lu et al. 2011). This effect forms a structure that is different from the original granulates. Amylose retrogrades in a time scale of hours, whereas amylopectin's retrogradation can take days, which causes starches of high-amylose content to retrograde faster (Kovrljia and Rondeau-Mouro 2017). Retrogradation is also advanced by minor acidity, increasing fat content, impurities and polyvalent ions, such as aluminum, calcium, sulfate and oxalate (BeMiller 2005). Ghost particles remaining from incomplete cooking can also assist retrogradation (Smits et al. 2003). In contrast, chemical modification (BeMiller 2005), short-chained amylopectin and high phosphorus-content deter retrogradation (Thygesen et al. 2003).

There are many differences among types of starch depending on their biological origin. Potato starch exhibits a peak viscosity during heating, which can be observed with a Brabender ViscoAmylograph. Other starches, such as wheat starch, exhibit a slow increase in viscosity during heating (BeMiller 2005). Potato starch requires a lower temperature to gelatinize than wheat starch, and the granules of potato starch disintegrate easily under heat and shear forces (Hermansson and Svegmärk 1996). Wheat starch has more fat and protein than potato starch, but potato starch has more phosphorus. Potato starch has more amylopectin and less amylose than wheat starch, and the amylose and amylopectin (Smits et al. 2003) chains of potato starch are longer than in wheat starch (Lehtinen 2000). Potato starch retrogrades less than cereal starches (Hermansson and Svegmärk 1996).

Many papers have been published on the use of ^1H NMR-relaxometry to study starch gelatinization and retrogradation (Baranowska et al. 2008, Bosmans et al. 2016, Lionetto et al. 2005, Wang et al. 2015). ^1H NMR-relaxometry is a technique that records the time required for protons to return to equilibrium after being exposed to a radio frequency pulse in a magnetic field (Bosmans et al. 2016). There are two main parameters measured by ^1H NMR-relaxometry, spin-lattice relaxation time T_1 , which is related to how spins interact with the environment, and spin-spin relaxation time T_2 , which is related to how spins interact with each other. Both relaxation times are related to the mobility of protons in a sample (Baranowska et al. 2008).

This study focuses on relaxation rate R_2 , which is the inverse of relaxation time T_2 . R_2 is larger for less mobile protons and smaller for protons that are more mobile (Lionetto et al. 2005). For starch solutions, the protons of water or gelatinized starch are more mobile than the protons of starch granules or retrograded starch (Wang et al. 2015). Thus, R_2 decreases as the starch becomes gelatinized, and

R_2 increases if the starch retrogrades (Lionetto et al. 2005). ^1H NMR-relaxometry studies of starch (Baranowska et al. 2008, Bosmans et al. 2016, Lionetto et al. 2005, Wang et al. 2015) have usually focused on unmodified starches used for foods, and the NMR-measurements have been conducted off-line. Publications about techniques for studying the chemically modified starches needed for paper-making or other applications are rarer. To the best of our knowledge, the gelatinization or retrogradation of starch has not been previously measured with on-line NMR-relaxometry.

The objective of this work was to study whether the gelatinization and retrogradation of cationic starch could be followed on-line, i. e., continuously, using ^1H T_2 NMR-relaxometry and to determine what type of differences would be detectable between potato starch and cereal starches (barley and wheat). Additional information regarding the cooking process of starch would be valuable for the paper industry because of the importance of properly dissolving starch before addition to a paper machine. Potato starch is used more often in papermaking than wheat starch because of its better performance, but wheat starch would be a cheaper option (Hermansson and Svegmärk 1996).

Materials and methods

Materials

The studied cationic starches were provided by Chemigate Oy, Finland, and the brand names of the starch products were Raisamyl 50021 (potato), Raisamyl 50051 (barley) and Raisamyl 50071 (wheat). The degree of substitution for all starches was 0.035. The method used for cationization by the supplier was dry cationization. The salts, NaCl and Na_2SO_4 , were purchased from Merck and J. T. Baker, respectively, and were of reagent-grade purity. Tap water at approximately 20 °C was used. Tap water was chosen because the water used in paper mills for starch cooking is also tap water.

NMR-equipment

On-line measurements of cationic starch samples were performed using a TD-NMR (time-domain NMR) system (Resonance systems ltd.) that was modified for flowing samples and automated (Nikolskaya et al. 2015). The ^1H resonance frequency of the system was 26 MHz, and the

temperature of the magnet was 30 °C. Spin–spin relaxation rates R_2 were measured by applying the Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence (Abragam 1961). The echo time was 6 ms, and the number of 180° pulses in the sequence was 600. The relaxation delay was 6 s, and the number of scans was equal to 4. The durations of the 90° and 180° RF pulses were 7 μ s and 16 μ s, respectively.

Measurements

The cooking procedure was based on the starch supplier's instructions. The starch consistency was always 5.0 % before heating, but due to some evaporation of water during the process, the consistency at the end of the cook was 5.3–5.6 %. The starch was added slowly to cool water (20 °C, 3.4 liters) with stirring. The solution was heated on a laboratory heating plate in a regular stainless steel kettle. The solution was kept at 91–96 °C for 30 minutes. Cooling was achieved by removing the heating plate. The heating rate was approximately 1.0 °C/min, and the cooling rate was approximately 0.7 °C/min. The measurement procedure was as follows:

- 1) A sample was continuously mixed at various temperatures in a container.
- 2) The sample was automatically pumped through the magnet system.
- 3) When a new sample was introduced to the system, the pump was stopped.
- 4) The CPMG signal was automatically measured and fitted using a mono-exponential function, and the R_2 value was solved.
- 5) The next sample was pumped.

A Matlab software script written by the authors was used to control the pump and TD-NMR measurements and to fit the CPMG signals. Temperature was measured from the kettle, so there is no data on the temperature of the solution measured inside the tube. The cooling inside the tube was assumed not to be significant enough to affect the measurements. The solution was pumped and measured once every 2 minutes. Each measurement was performed only once to save time and to minimize cooling inside the tube. During the cooling period and before reaching 60 °C, samples were added to test tubes and stored at 8, 20 and 60 °C to study the effect of storage temperature and storage time on retrogradation. The test tubes were measured quickly after taking them from storage to minimize temperature changes in the samples.

Results and discussion

Potato starch cook

The obtained NMR-relaxation curve for the heating–holding–cooling cycle of cationic potato starch is shown in Figure 1. The first points at the beginning of the heating curve ($R_2 \approx 0.8 \text{ s}^{-1}$ and $T \approx 20 \text{ °C}$) were measured from water only, and this applies to other measurements as well. The addition of starch caused a rapid increase of the R_2 , which indicates an increase in the amount of less mobile protons in the solution. As heating began, R_2 stayed rather constant, but at 50 °C it began to decline. This can be interpreted as the beginning of gelatinization.

Figure 1: Heating–holding–cooling cycle for Raisamyl 50021 potato starch with 5 % consistency.

Over the temperature range of 52 to 74 °C, the solution became more viscous. A spoon was needed to help mix the solution due to its high viscosity. Near 74 °C, the solution's viscosity began to decline, and stirring continued normally. This observation is in line with literature reports, in which a viscosity peak is described for potato starch (Be-Miller 2005). The change in viscosity is not visible in the NMR-relaxation curve.

When the solution reached 95 °C, the R_2 had declined to the same level as in pure tap water. This was interpreted to mean that starch had fully gelatinized and that there were no longer any crystalline or amorphous structures present, which would contain less mobile protons. As the solution cooled, R_2 remained at the same level as that in water. This was interpreted to indicate that the starch stayed gelatinized and retrogradation did not occur. Visually the solution was clear during cooling, which can be interpreted to indicate full gelatinization.

Figure 2: Heating-holding-cooling cycle for Raisamyl 50051 barley starch with 5 % consistency.

Figure 3: Heating-holding-cooling cycle for Raisamyl 50071 wheat starch with 5 % consistency.

Barley starch cook

As seen from Figure 2, the NMR-relaxation curve for cationic barley starch is clearly different from that of potato starch. The first points in the heating curve are for water only, as in Figure 1. The beginning of the heating curve was similar to that of potato starch, but R_2 began to increase with heating instead of staying rather constant. R_2 began to decrease near 50 °C, which also occurred for potato starch, but in the case of barley starch, R_2 never decreased to the level of water. It was observed that the solution did not become as clear as the potato starch solution. As cooling began, R_2 began to increase immediately, and the cooling curve followed the shape of the heating curve up to 65 °C.

From these results, it can be argued that the cooking of barley starch is not completely finished, i. e., the starch is not fully gelatinized. The ungelatinized starch particles, or ghost particles, likely cause the starch to retrograde rapidly as soon as the temperature begins to fall. At the end of the cooling curve ($T = 45$ °C), R_2 is at the same level as when starch was first added to the water.

Barley starch did not become highly viscous during cooking, as did the potato starch. Instead, the viscosity increased slowly with increasing temperature, but the solution never became very viscous. This is in line with previously reported literature data (BeMiller 2005).

Wheat starch cook

The NMR-relaxation curves for wheat starch and barley starch are quite similar, as expected because they are both cereal starches. In Figure 3, the heating R_2 curve for wheat starch also begins to increase and then decreases until the cooking temperature is reached, but R_2 never declines to the level of water. Cooling showed the same phenomenon

as seen for barley, where ghost particles likely cause an increase in R_2 , which means that the starch undergoes rapid retrogradation. From this, it can be argued that the cooking for wheat is also unfinished, i. e., the starch is not fully gelatinized. The cloudiness and viscosity were similar to that observed in barley starch.

Effect of NaCl and Na_2SO_4 on the cook

Finally, the effect of sodium chloride NaCl and sodium sulfate Na_2SO_4 on wheat starch cooking was tested. These salts were chosen because they were mentioned in the literature as being able to inhibit the gelatinization of starch (Maurer 2007). Wheat starch was chosen because it did not gelatinize completely, so possible changes in gelatinization behavior may be more visible in it than in fully gelatinized potato starch.

Figure 4: Heating-holding-cooling cycle of Raisamyl 50071 wheat starch with 2 % NaCl and without additive.

As seen from Figure 4, adding 2 % NaCl to the cooking solution (relative to the dry mass of starch) does not affect the R_2 curve significantly. It appears that R_2 is slightly

Figure 5: Heating-holding-cooling cycle of Raisamyl 50071 wheat starch with 10 % Na_2SO_4 and without additive.

higher for the solution with NaCl than without it during holding at 95 °C, which could indicate that the salt inhibits gelatinization, but the effect is small.

Next, adding 10 % of Na_2SO_4 (in relation to the dry mass of starch) to the cooking solution was studied. A larger amount of a divalent salt, such as sulfate, was speculated to show a larger effect than a smaller amount of a monovalent salt, such as NaCl. However, the result seen in Figure 5 is highly similar to that of adding 2 % NaCl.

Storage of cooked starch

Samples were taken from all cooking batches and stored at 8, 20 or 60 °C. In Figure 6, the potato starch solution kept at 60 °C for 9 days had the same R_2 value as water ($R_2 \approx 0.8 \text{ s}^{-1}$), so it likely did not experience retrogradation. The potato starch samples stored at 8 and 20 °C, however, clearly underwent some retrogradation because their R_2 values increased. Visually, the potato starch sample stored at 60 °C was still clear and had a low viscosity after 9 days, whereas the sample stored at 8 °C was cloudy and highly viscous. The sample stored at 20 °C had visual and viscous properties, which were between those of the samples at 8 and 60 °C.

Barley starch was similar to potato starch; R_2 of the sample stored at 60 °C remained almost at the original level ($R_2 \approx 2.5 \text{ s}^{-1}$) when it was taken from the cooking solution at approximately 60 °C. The barley starch samples stored at 8 and 20 °C are clearly different from the corresponding potato starch samples. The barley starch sample stored at 8 °C retrograded to a larger extent than the sample stored at 20 °C, whereas for potato starch both samples had nearly the same R_2 . All barley starch samples were visually cloudy and highly viscous. Wheat starch behaved

Figure 6: R_2 values of starch solutions after 9 or 13 days of storage at 8, 20 or 60 °C.

very similarly during storage to barley starch; R_2 were similar, and visually the samples were similar.

The wheat starch solutions containing NaCl or Na_2SO_4 salts were measured more precisely over time than the aforementioned samples, which were measured only once. From Figure 7, it can be seen that there seems to be a tendency for the samples with 2 % NaCl to have higher R_2 values than the samples with 10 % Na_2SO_4 at all storage temperatures. Wheat starch with no salt (Figure 6) had the highest R_2 value (about 4.5 s^{-1}) for samples stored at 8 °C. Thus, increasing ionic strength appeared to decrease the amount of retrogradation for samples stored at 8 °C.

Figure 7: R_2 values of stored Raisamyl 50071 wheat starch solutions with 2 % NaCl or 10 % Na_2SO_4 at various temperatures over time.

R_2 for samples stored at 20 °C began to decrease with storage time, which was unexpected. Retrogradation was anticipated to advance or stop at room temperature but not to be reversible. One explanation could be that the starch begins to degrade at room temperature due to bacteria or fungi present in the test tubes. For samples stored at 60 °C, R_2 stayed nearly constant for the entire observed period.

This indicates that 60 °C is a good temperature for storing wheat starch because the starch neither retrogrades nor degrades.

In summary, NaCl and Na₂SO₄ did not have a significant effect on the gelatinization of cationic wheat starch, but the salts did have an effect on retrogradation. Visually, the wheat starch solutions containing salts stored at 60 °C were less viscous than the wheat starch solution without salts stored at 60 °C. Cloudiness was the same for all solutions with or without salt. For the solutions stored at 8 or 20 °C, there was no visual difference in viscosity with or without salt.

Conclusions

¹H NMR R₂-relaxometry was successfully utilized to measure the gelatinization of cationic potato, barley and wheat starch on-line. It was possible to determine whether the starch had gelatinized completely during heating or if the cook was incomplete. During cooling of the solution, it was observed that completely dissolved starch remained gelatinized but partially dissolved starch underwent rapid retrogradation. NMR-relaxometry could also be used to monitor starches stored at various temperatures to observe whether they retrograde.

Clear differences were observed between the gelatinization and retrogradation of potato starch and cereal starches. Potato starch dissolved completely during cooking at 95 °C at normal pressure and remained gelatinized when the solution cooled. Cereal starches dissolved only partially during cooking and underwent rapid retrogradation during cooling. It can be concluded that complete gelatinization of starch is necessary for it to stay gelatinized when stored at 60 °C.

Storage of cooked cationic starch at 60 °C was shown to maintain a constant R₂ value when the sample was originally taken from the solution at approximately 60 °C. Storing starch at 60 °C stopped retrogradation from advancing for all starches. NaCl and Na₂SO₄ did not have a major effect on the gelatinization of wheat starch but did retard its retrogradation.

Based on these findings, ¹H NMR R₂-relaxometry has potential as a tool in paper mills for quality control during cooking and storage of cationic starch solutions before their addition to a paper machine. In future studies, it would be good to link NMR-relaxometry data with other measurement tools to further confirm the dependency between degrees of gelatinization and retrogradation with R₂.

Acknowledgments: Jenna Raunio would like to thank RDI Specialist Emmi Kallio for providing support and tips for this writing process.

Funding: This research was funded as part of a larger research project (PURE – Clean reactor and process technology for bioproduct manufacturing – journal number 1343/31/2017) by TEKES – the Finnish Funding Agency for Innovation, European Regional Development Fund (ERDF) and partner companies. The partner companies were Altum Technologies Oy, Andritz Oy, Ceresto Oy, Chemigate Oy, Janesko Oy, Kemira Oyj, Ket-Met Oy, Pixact Oy, Stora Enso Oyj, UPM-Kymmene Oyj and Wetend Technologies Oy. The funding sources were not involved in the study design or in the collection, interpretation or analysis of the data.

Conflict of interest: The authors declare no conflict of interest.

References

- Abraham, A. The Principles of Nuclear Magnetism. Clarendon Press, Oxford, 1961.
- Baranowska, H. M., Sikora, M., Kowalski, S., Tomasik, P. (2008) Interactions of potato starch with selected polysaccharide hydrocolloids as measured by low-field NMR. Food Hydrocoll. 22(2):336–345. <https://doi.org/10.1016/j.foodhyd.2006.12.014>.
- BeMiller, J. Starch in the Paper Industry. Starch: Chemistry and Technology. Elsevier Science, San Diego, 2005.
- Bosmans, G. M., Pareyt, B., Delcour, J. A. (2016) Non-additive response of blends of rice and potato starch during heating at intermediate water contents: A differential scanning calorimetry and proton nuclear magnetic resonance study. Food Chem. 192:586–595. <https://doi.org/10.1016/j.foodchem.2015.07.056> Supplement C.
- Hermansson, A., Svegmark, K. (1996) Developments in the understanding of starch functionality. Trends Food Sci. Technol. 7(11):345–353. [https://doi.org/10.1016/S0924-2244\(96\)10036-4](https://doi.org/10.1016/S0924-2244(96)10036-4).
- Kovrlja, R., Rondeau-Mouro, C. (2017) Hydrothermal changes in wheat starch monitored by two-dimensional NMR. Food Chem. 214:412–422. <https://doi.org/10.1016/j.foodchem.2016.07.051> Supplement C.
- Lehtinen, E. Papermaking Science and Technology, Book 11: Pigment Coating and Surface Sizing of Paper. Fapet Oy, Finland, 2000.
- Lionetto, F., Maffezzoli, A., Ottenhof, M., Farhat, I. A., Mitchell, J. R. (2005) The retrogradation of concentrated wheat starch systems. Starch – Stärke 57(1):16–24. 10.1002/star.200400298.

- Lu, S., Chen, J., Chen, Y., Lii, C., Lai, P., Chen, H. (2011) Water mobility, rheological and textural properties of rice starch gel. *J. Cereal Sci.* 53(1):31–36. <https://doi.org/10.1016/j.jcs.2010.08.006>.
- Maurer, H. W. *Starch and Starch Products for Wet End Applications*. TAPPI, 2007.
- Neimo, L. *Papermaking Science and Technology, Book 4: Papermaking Chemistry*. Fapet Oy, 1999.
- Nikolskaya, E., Liukkonen, M., Kankkunen, J., Hiltunen, Y. (2015) A non-fouling online method for monitoring precipitation of metal ions in mine waters. *IFAC – PapersOnLine* 48(17):98–101. <https://doi.org/10.1016/j.ifacol.2015.10.085>.
- Ritola, M., Gianferri, R., Bucci, R., Brosio, E. (2008) Proton NMR relaxation study of swelling and gelatinisation process in rice starch–water samples. *Food Chem.* 110(1):14–22. <https://doi.org/10.1016/j.foodchem.2008.01.048>.
- Smits, A. L. M., Kruiskamp, P. H., van Soest, J. J. G., Vliegenthart, J. F. G. (2003) The influence of various small plasticisers and malto-oligosaccharides on the retrogradation of (partly) gelatinised starch. *Carbohydr. Polym.* 51(4):417–424. [https://doi.org/10.1016/S0144-8617\(02\)00206-0](https://doi.org/10.1016/S0144-8617(02)00206-0).
- Stenius, P. *Papermaking Science and Technology, Book 4: Papermaking Chemistry*, 2nd edn. Paperi ja Puu Oy, Finland, 2007.
- Thygesen, L. G., Blennow, A., Engelsen, S. B. (2003) The effects of amylose and starch phosphate on starch gel retrogradation studied by low-field ^1H NMR relaxometry. *Starch – Stärke* 55(6):241–249. 10.1002/star.200390062.
- Wang, S., Li, C., Copeland, L., Niu, Q., Wang, S. (2015) Starch retrogradation: A comprehensive review. *Compr. Rev. Food Sci. Food Saf.* 14(5):568–585. 10.1111/1541-4337.12143.