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# Multi-scale NMR and MRI approaches to characterize starchy products

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ABSTRACT

This review deals with the use of Nuclear Magnetic Resonance techniques to monitor the behavior of starch as well as the migration and distribution of water during the processing or storage of starchy matrices. The aim is to emphasize the potentials of NMR techniques for the quantitative characterization of water transfers in starch-water systems on different length scales. Relaxation and self-diffusion experiments using low-field NMR spectrometry provided important information on the relationship between water dynamics and the microscopic organization of starch granules at various temperatures and water contents. Some works dealt with the botanical origin of starch but also the impact of possible additives. Indeed, the investigation on model starch-based systems was recently expanded to more complex real systems, including dough, bread, cakes, spaghetti and lasagna. Two-dimensional (2D) cross correlation methods have also been developed to elucidate chemical and diffusional proton exchange phenomena, and to improve the interpretation of results obtained in 1D. Finally, magnetic resonance micro-imaging methods were developed to study or to quantify water intake into starch-based matrices.

## 1. Introduction

Understanding the structure of food enables the engineering of their specific nutritional, physical, and sensorial properties (Koc, Vinyard, Essick, & Foegeding, 2013). However, foods, and in particular wheat cereal products consist of complex multiphasic biopolymer matrices that interact strongly with water, thereby complicating the prediction of the food's properties and behavior. These matrices are heterogeneous at the microscopic scale, which affects their macroscale properties. Most changes in foods, including changes in their composition, structural and mechanical properties, are caused by diffusive processes in one form or another that occur at different scales and include both water and biomolecules. Amongst the latter, starch is one of the major components of cereal foods. The properties of starch and interactions with other constituents, particularly with water, are of great interest to the food industry (Delcour et al., 2010). Moreover, phase transitions in starch have a major influence on the physical properties and stability of food matrices. Therefore, many manufactured food products involves the gelatinization of starch (pasta and pre-cooked rice, breads and industrial pastries) along with drying and grinding to obtain pre-gelatinized forms that are widely used as thickeners in the food industry. In the presence of small amounts of water and at high temperatures (above 130 °C for water contents <20%), extrusion makes it possible to manufacture snacks or cereals. To make better use of the textural properties of starchy foods and to improve their preservation, it is necessary to understand the changes that occur in such matrices during heat and moisture treatments, as well as in subsequent cooling and storage.

Food companies make use of several types of starch, with different properties originating from their biosynthesis and different characteristics of starch production and processing. Starches from different botanical origins can be distinguished by their amylose-to-amylopectin ratio, granule size and morphology, and starch polymorphism. Their functionality and the stability in many starch-based food products are intimately related to their hydration level and the thermomechanical processes applied to transform them. Starch processing involves a number of structural changes. When starch is heated in presence of a sufficient amount of water, the loss of molecular order in starch structure and the amylose leaching result in the conversion of an aqueous suspension of starch granules into a viscous paste, i.e. gelatinization (Delcour et al., 2010). In the phase following gelatinization, i.e. pasting phase, the amorphous regions play a significant role through the further leaching of carbohydrate material. Cooling the system implies the formation of a three-dimensional starch network of leached material (Atwell, Hood, Lineback, Varriano-Marston, & Zobel, 1988). When the leached amylose crystallizes into double helices in the continuous phase, this process is referred to as gelation. The amylose chains readily associate during the

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initial (<24 h) stage of storage, whereas during the latter stage (>24 h) the process of recrystallization of amylopectin, namely retrogradation, becomes the dominant process (Lewen, Paeschke, Reid, Molitor, & Schmidt, 2003).

Nuclear Magnetic Resonance (NMR) is a powerful tool for elucidating chemical structure, molecular dynamics and interactions of compounds ranging from small organic molecules to minerals and protein complexes (see references in (Marcone et al., 2013)). Since the discovery of the method in 1948, several analytical techniques have emerged, including NMR spectroscopy and NMR imaging called MRI. The coverage of different length scales by NMR and MRI helps understand the structure of food and its constituents (Mariette, 2009). However, because of complexity of foodstuffs and the low sensitivity of the NMR method, the molecules are often extracted prior to analysis. NMR is complementary to other analytical techniques, including X-ray diffraction, rheology and calorimetry, for the characterization of starch systems.

Thanks to its non-destructive and non-invasive nature, speed and ease of use, the time domain NMR (TD-NMR) method is highly appreciated by the food industry, especially for quality control of moisture and solid fat content (ISO, 1991). TD-NMR has also been used for decades for research on starch polysaccharides, as evidenced by the numerous relaxometry and diffusometry studies ($T_1$ and $T_2$ relaxation, Diffusion or D measurements, for a further description see below). These investigations were conducted on both water and starch in model systems as well as in complex food matrices, such as dough, bread and cakes. NMR relaxation is also a convenient method for the continuous monitoring of products during processing up to their final structure (Mortensen, Thybo, Bertram, Andersen, & Engelsen, 2005; Rondeau-Mouro et al., 2015). These goals have been achieved by measuring the relaxation times and self-diffusion coefficients mainly of water protons but also of starch protons. Although NMR relaxometry is a unique technique in providing information on the changes in microscopic distribution of water within and outside the starch granules, assigning the relaxation times remains a major difficulty. Two-dimensional NMR ($T_1$-$T_2$ and D-$T_2$) methods have been used to overcome this challenge thanks to their enormous potential for characterizing complex systems by measuring $T_1$ and $T_{2,}$ as well as D and $T_2$, in joint encoding (Hills, Costa, Marigheto, & Wright, 2005; Serial et al., 2016; Tønning, Polders, Callaghan, & Engelsen, 2007).

Finally, the use of MRI for the characterization of heterogeneous products like food products is in progress, in particular micro-imaging methods using high-field NMR spectrometers equipped with a xyz-gradient system for localized measurements (Bonomi et al., 2012; Horigane et al., 2006; McCarthy, Gonzalez, & McCarthy, 2002; Sekiyama et al., 2012).

Understanding the relationships between micro- and macroscopic scales usually requires a large number of destructive experiments. For this reason, we propose new multi-scale non-destructive characterization to continuously relate the microstructure and the macroscopic properties of starch-based matrices. The approach is based on NMR relaxometry, self-diffusion and mutual diffusion measurements, which cover distances ranging from the molecular to the macroscopic. Investigating starch using this method has many advantages because of the complex organization of carbohydrate chains of amylopectin and amylose within starch granules (at the microscale) and transport properties of the matrix (at the macroscale). As both liquid- and solid-state high-resolution NMR methods failed to provide information about the distribution of water among the various micro-phases that form complex biopolymer systems, these topics are not covered in this review. The present review focuses on how starch and water behave during the classical processing methods used in the food industry, monitored using NMR techniques with no chemical preparation of the samples. Before reporting published studies on the subject, we first recall the basic principles of the measured physical phenomena. The aim is to considerably advance our understanding of the changes in starch-water mixtures caused by processing and storage using NMR relaxation and self-diffusion (mobility of microscopic local water) and MR micro-imaging (macroscopic water migration) measurements.

## 2. Relaxation measurements in starch-based matrices

NMR relaxation involves the processes whereby, after absorption of the radiofrequency energy, the excited nuclei (protons) in the sample return to thermal equilibrium through energy release and exchange with the surrounding lattice. NMR signal is commonly analyzed in terms of two separate processes, each with their own time constants; spin-lattice ($T_1$) relaxation involves a transfer of energy between the spin system and the environment, whereas spin-spin relaxation ($T_2$) processes are entropic processes that involve the dephasing of nuclear spins. The relaxation process occurs through fluctuations in magnetic field due to random molecular motions, both rotational and translational. The rate and the nature of these motions affect the NMR signal decay, which is measurable through $T_1$ and $T_2$ relaxation times (Blumich, Casanova, & Appelt, 2009). Each chemically different species possesses nuclei that have specific relaxation parameters, and depending on the nature of the species, $T_1$ and $T_2$ values may differ considerably. Relaxation parameters in a given spin system depend not only on structural information (through the interactions themselves), but also on dynamic information (through the geometry and time scale of molecular motion). Due to the different nature of the molecules, their environment and their interactions, the recorded NMR signal is the combination of the contributions of all the nuclei that relax differently. But the multi-component signal can also be observed for a single molecule type but localized in various regions (proton compartments) of the sample, or in interaction/exchange with other molecules. This is the case for water molecules in complex samples like foods and more generally in starch-based matrices.

### 2.1. $T_1$ of starchy systems

Although much research has been conducted on the mobility (dynamics) of starch-water systems, few data are available on their $T_1$ proton relaxation time. These investigations were mainly performed in low magnetic fields and usually consisted of varying the measurement temperature, the water content or a combination thereof. These experimental conditions imitate what happens during the preparation of starch-containing food, when starch gelatinization involves heating in water resulting in the formation of a gel. As mentioned in the introduction, gelatinization and retrogradation abilities are the principal factors that control the texture and quality of starch-containing food products. These transformations were investigated in samples with intermediate or high level of hydration.

#### 2.1.1. Intermediate and high hydration levels

The water-dependent behavior of starch was monitored using a 15 MHz NMR spectrometer to analyze corn starch mixtures with 67, 50 and 33% of water (calculated on a wet weight basis-wb) at 30, 60 and 80 °C (Cornillon & Salim, 2000). As shown in Fig. 1, a single $T_1$ relaxation time was measured, indicating fast exchanges between bulk water and water associated with starch polymers. According to the authors, at 60 °C $T_1$ curves presented a minimum due to the swelling of granules by water uptake, decreasing the overall mobility of the system. A slight decrease in $T_1$ relaxation time with increasing temperature has also been reported in starch