NMR relaxometry and micro-imaging of starchy products

C. Rondeau-Mouro
R. Kovrlija

MR-Food, IRSTEA Rennes, France
Develops **quantitative NMR and MRI** methods for the characterization of bioproducts and their processing.

**Multi-scale and dynamic approaches**
- Molecular, tissue, product scales
- Real-time measurements while product is processed

Contributes to the optimization of the food quality, of the food processing by reducing environmental impacts.
RESEARCH AIMS

- Understand and quantify **water migration** in starch-based products
- Innovation and optimization of **industrial processes** through an understanding of phenomena of transfer of matter at microscopic and macroscopic scales (baking, water-uptake of materials)
STARCH APPLICATIONS

Basis of many food and non-food products

Use of Starch

- Contributes to texture, viscosity, gel formation, adhesion, binding, moisture retention, film formation, and product homogeneity
- Only a small portion of starch is used in its native state
- Complex structure - function relationship
Diversity in:

- Size, morphology and A/B ratio
- Crystalline polymorphs

HYDROTHERMAL TRANSFORMATIONS

T < Tgel

- Diffusion of water
- Reversible swelling
- Amylose leaching

T > Tgel

- Irreversible swelling
- Melting of crystals
- Disintegration of granules

1D NMR – $T_2$ RELAXATION MEASUREMENTS

Starch-Water (45%, wb) 20 MHz  $T=20^\circ C$

Assignment of $T_2$ components:

3 – intra-granular water protons
4 – extra-granular water protons

Lack of data:

- at INTERMEDIATE water content (25-60%, wb)
- For starch
- Upon heating (DYNAMICAL STUDY)
1D NMR – $T_2$ RELAXATION MEASUREMENTS

Starch-Water (45%, wb) 20 MHz  T = 20°C

Coupling of FID and CPMG sequences to quantify the liquid and solid phases in sample

- getting a **better time resolution** in the microsecond $T_2$ range
- interpreting the **changes in intensity** of each $T_2$ component in term of structural changes or proton exchanges between each proton fraction
DYNAMIC MEASUREMENTS

Starch-Water (35, 40, 42, 45 and 50 %, wb)

Assignment of $T_2(1)$ and $T_2(2)$

1 – non-exchangeable starch (amylopectin + amylose) protons
2 – non-exchangeable amylose protons
3 – intra-granular water protons
4, 5 – extra-granular water protons
**T₁ STUDIES ON STARCHY MATRICES**, not much study

High hydration levels (≥ 60%, wb)
- Rice starch (Fan et al. 2013), waxy maize, corn, and potato starch (Gonera and Cornillon, 2002), potato, oat, cassava and corn starch (Baranowska et al., 2008, 2011), wheat starch (Callaghan et al., 1983), and rice flour (Ritota et al., 2008)

Intermediate hydration levels (25-60%, wb)
- Corn starch (Cornillon and Salim, 2000), dough (Kim and Cornillon, 2001) and bread (Curti et al., 2011)

Corn starch - Water (25-40%, wb)

*Only one T₁ relaxation time assigned to water in interaction with starch*

2D (T<sub>1</sub>-T<sub>2</sub>) acquisition and MEM processing

IR-CPMG

2D Laplace inversion by 2D Fredholm integral of the first kind

\[
k = \left(1 - 2e^{-\tau_1/T_1}\right)e^{-\tau_2/T_2}
\]

\[
Y(\tau_1, \tau_2) = \int\int \left(1 - 2e^{-\tau_1/T_1}\right)S(T_1, T_2)e^{-\tau_2/T_2}dT_1dT_2
\]

- Convergent iterative reconstruction method based on **maximum entropy regularization**
- Minimization by Truncated Newton algorithm
- Prior knowledge on the range of expected values of T<sub>1</sub> and T<sub>2</sub>
- Kernel separability and positivity constraint

Acquisition and processing of 2D IR-FID-CPMG (T₁-T₂)

\[ k_2(\tau_2, T_2) = \begin{cases} 
\alpha \left( e^{-\frac{\tau_2}{T_1}} + e^{-\frac{\tau_2^2}{T_2}} \right) \cdot \text{sinc} \left( \frac{\omega}{T_2} \cdot \tau_2 \right) & \text{if } \tau_2 \leq \tau_{fid} \\
(1 - \alpha) e^{-\frac{\tau_2}{T_2}} & \text{if } \tau_2 > \tau_{fid} 
\end{cases} \]

\[ k_1(\tau_1, T_1) = 1 - \gamma \cdot e^{-\frac{\tau_1}{T_1}} \]

- Fitting of FID data using gaussian*sinC
- Variation of \( \gamma \)
- Quantification of T₁ and T₂ components

Quantitative 2D IR-FID-CPMG \( (T_1 - T_2) \)

\[
k_2(\tau_2, T_2) = \begin{cases} 
\alpha \left( e^{-\frac{\tau_2}{T_1}} + e^{-\frac{\tau_2}{T_2}} \right) \cdot \text{sinc} \left( \frac{\omega}{T_2} \tau_2 \right) & \text{if } \tau_2 \leq \tau_{\text{fid}} \\
(1 - \alpha) e^{-\frac{\tau_2}{T_2}} & \text{if } \tau_2 > \tau_{\text{fid}} 
\end{cases}
\]

\[
k_1(\tau_1, T_1) = 1 - \gamma e^{-\frac{\tau_1}{T_1}}
\]

\[
S(T_1) = \int S(T_1, T_2) \, dT_1
\]

\[
S(T_2) = \int S(T_1, T_2) \, dT_2
\]

2D NMR $T_1$-$T_2$ of wheat starch-water at 45 % wc

$\text{SC (\%)} = \frac{I_{T_2(1)} + I_{T_2(2)}}{m_{\text{sample}}/m_{\text{starch}}}$

- $[T_1, T_2]$
  - $[147, 0.019]$
  - $[147, 0.101]$
  - $[147, 2.1]$
  - $[147, 14.4]$

- $[T_1, T_2]$
  - $[229, 0.018]$
  - $[229, 0.117]$
  - $[229, 1.8]$
  - $[229, 13.9]$

- $[T_1, T_2]$
  - $[64, 48]$
  - $[38, 0.117]$
  - $[38, 1.8]$

20°C

SC = 59.1 ± 1.3 %

90°C

Starch gelatinisation

SC = 20.4 ± 1.7 %

50 values of $\tau_1$ times between 5 ms and 1500 ms, 800 echoes using echo time $\tau_2$ of 0.2 ms, RD = 1.5 s. $\varphi = 172^\circ$

Number of iterations 1000; $\omega = 0$ rad; $kh^2 0.3267$ at 293 K and 0.3769 at 323 K; RMSE 0.0114 at 293 K and 0.0083 at 323 K.
Cross relaxation

- This process includes several simultaneous mechanisms
  
  i) **dipolar couplings**, which are magnetization transfers through space between protons at a distance of less than 1 nm,

  ii) **chemical exchange** of protons typically observed between free solvent and a labile solid matrix and

  iii) **molecular exchange** of a solvent between compartments.

Can we use the amplitude of the short $T_1$ due to cross-relaxation phenomena as an indicator of the gelatinization extent?

2D NMR $T_1$-FID-CPMG = a quantitative method

**Dough (45% wc)**

- **20°C before baking**
  - SC = 53.3 ± 0.3%

- **20°C after baking**
  - SC = 64.14 ± 2.5%

1-Baking → 2-Cooling

**AMF-water**

- **6°C**
  - SFC = 56.3 ± 2.3%
  - Water content = 20.23 ± 0.36%

**Gravimetry** 19.42 ± 0.08%
NMR / MRI

- Optimal signal acquisition
- Short echo times (0.5 ms or less)
- Large number of points

MRI
- $T_2$ mapping with spatial encoding
- Less optimal signal sampling due to gradients encoding
- Relaxation times on the whole sample

$T_{2\min} \geq 2\text{ms}$
Potato starch-glycerol blends, 4mm Ø

Shape-memory property:

- **500 MHz**
- MSME
- $\Delta T_E$ of 5 ms, 32 echoes
- $T_R = 1.5$ s, $A_Q = 15$ min
- $128 \times 128$, FOV $10 \times 10$ mm
- Resolution = (78 $\times$ 78 $\mu$m$^2$)$^*500$ $\mu$m

$T_2$ (ms)
PROTON DENSITY & $T_2$ CHANGES

$d_1 = 0$ mm

$d_2 = 2.31$ mm

After 3 weeks

Initial specimen

A. Beilvert et al. / Carbohydrate Polymers 99 (2014) 242–248
Crank defined diffusion models for several sample geometries, such as plane sheet, infinite cylinder and sphere.

Concentration of water in a cylinder:

\[
\frac{I - I_0}{I_\infty - I_0} = 1 - \frac{2}{r} \sum_{n=1}^{\infty} \frac{e^{-D\alpha_n^2t}J_0(x\alpha_n)}{\alpha_n J_1(r\alpha_n)}
\]


R. Kovrlja, C. Rondeau-Mouro Multi-scale NMR and MRI approaches to characterize starchy products, Food Chemistry, in press
**TRANSPORT DIFFUSION COEFFICIENT OF WATER**

Calculation of $\bar{D}$ the average diffusion coefficient

\[
\frac{I_t}{I_\infty} = k \ t^n
\]

\[
\bar{D} = \left( \frac{\pi kr}{4} \right)^2
\]

\[
\bar{D} = (3.7 \pm 1.0) \times 10^{-10} \text{ m}^2/\text{s}
\]

$n=0.48 \pm 0.03$

Case I kinetics - Fickian Diffusion ($n \sim 1/2$)

$\nu$ water diffusion $<< \nu$ starch relaxation
RADIAL SWELLING OF STARCH BLENDS

Immersion time
22h

T=22°C

Diameter (mm)

\[ d = d_{\text{max}} - c \cdot e^{-k_s t} \]

\[ d_{\text{max}} = 5.885 \pm 0.009 \text{ mm} \]

\[ c = 0.907 \]

\[ k_s = 5.209 \times 10^{-3} \text{ min}^{-1} \]

Swelling rate
25.6 \pm 0.2\%

R. Kovrlija, C. Rondeau-Mouro Multi-scale NMR and MRI approaches to characterize starchy products, Food Chemistry, in press
Acknowledgements

- Ruzica Kovrlija PhD
  *Irstea, UR OPAALE, Rennes, France*

- Dr. Denis Lourdin
  *INRA UR BIA, Nantes, France*

- Prof. Said Moussaoui
  *IRCCYN, CNRS UMR 6597, Ecole Centrale, Nantes, France*
European Network on NMR Relaxometry

COST (European Cooperation in Science and Technology) is a pan-European intergovernmental framework. Its mission is to enable break-through scientific and technological developments leading to new concepts and products and thereby contribute to strengthening Europe’s research and innovation capacities.

The author would like to acknowledge networking support by the COST Action CA15209