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Magnetic resonance imaging (MRI) to quantify the swelling and drying of whey protein hydrogels

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ABSTRACT

Magnetic resonance imaging (MRI) is a very powerful technique increasingly used in food engineering, yet examples where the local water content is quantified are scarce. Homogeneous whey protein hydrogels were utilized as a model system, far simpler than most foods. The normalized proton density intensity of hydrogels was predicted using experimental correlations of the spin-lattice and spin-spin relaxation times, T_1 and T_2 respectively. Using a typical echo time T_E of 20 ms, the intensity is maximum at a volumetric swelling ratio Q ~15, and MRI is suitable to study the drying of hydrogels at lower Q values. Swelling can be studied by adjusting T_E to target the Q range of interest, e.g. ~200 ms. Whereas reasonable agreement is found between predicted normalized intensities and from drying and swelling experiments, local quantification of Q in unknown conditions will suffer from noise and relatively poor repeatability. Deviations from predictions are observed in the swelling at high NaCl concentrations, and at high alkaline pH, that need to be studied further. Opaque particulate hydrogels can be studied equally well compared to stranded transparent gel, a clear advantage against optical techniques.

1. Introduction

Magnetic resonance imaging (MRI) has been extensively used in recent years in all kinds of foods, as reviewed elsewhere (Kirtil and Oztop, 2016; Marcone et al., 2013; Patel et al., 2015). High-field MRI, which provide high signal-to-noise ratios, can provide in some cases better results than low-field MRI (Magee et al., 2003), but its capital and maintenance costs are usually very high, in food engineering and in many other disciplines, thus the continuous desire to use and develop less powerful magnets (Sarracanie et al., 2015). One of the most interesting uses of proton (^{1}H) MRI is to quantify the local water distribution, as is commonly performed in pharmaceutical research (Mantle, 2011), for example in the dissolution of tablets in water (Chen et al., 2010).

Comparable water mass transfer problems are equally important in foods, during their processing and storage, hence the extensive recent use of MRI. However, most studies do not quantify in absolute terms the water content in the samples, and many times only qualitative information is obtained from MRI images, for example in sandwiches (Ramos-Cabrer et al., 2006), beef (Bouhrara et al., 2012), bread (Li et al., 2012), pasta (Pasini et al., 2015); or in food hydrocolloids such as xanthan-curdlan (Williams et al., 2011), chitosan (Goycoolea et al., 2011), gelatin (Frutos et al., 2010), and konjac glucomannan-egg white hydrogels (Liu et al., 2013). Qualitative comparisons between the MRI intensity and gravimetric experiments during drying are reported in the literature (Ishida et al., 2004), but few calibration curves have been determined experimentally, for example in cheese (Altan et al., 2011) or pasta (Irie et al., 2004), to be used for the local quantification of water.

Quantification of water in solids using MRI is typically performed as follows. The signal intensity S in a conventional spin-echo MRI image depends on the sample dependent spin-lattice and spin-spin relaxation times, T_1 and T_2 respectively, together with the machine adjustable T_E and T_R, the echo time and the repetition time of the sequence (Fyfe and Blazek, 1997):

$$S(\phi) = S_0(1-\phi)\exp(-T_E/T_2)(1-\exp(-T_R/T_1)) \quad (1)$$

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where φ is the volume fraction of the solid material (polymer, protein, etc) in the voxel, and S_0 is the maximum signal intensity determined by proton density and instrumental factors (Chen et al., 2008). T_E and T_R are normally chosen in order that the second and third terms are close to unity, hence $T_E \ll T_2$ and $T_R \gg T_1$. In practice, there are limits to this simplification particularly if we want to quantify systems with large amounts of water (Barros et al., 2012). Researchers simplify this problem by experimentally finding the relationship between T_1 and T_2 with the solid content (or more accurately, to the fraction of water bounded to the solid), for example:

$$\frac{1}{T_i} = \left(\frac{1}{T_i}\right)_f + A_1\phi + A_2\phi^2 \quad (2)$$

where A_1 and A_2 are material dependent parameters, and $(1/T_i)_f$ is the proton relaxation for free water. A linear relationship is commonly observed at low solid contents, and the parameter A_1 would correspond to the proton relaxation rate of bound water $(1/T_i)_b$ (Barros et al., 2012; Baumgartner et al., 2005; Chen et al., 2008), but it not necessary holds at high solid concentrations (Fyfe and Blazek, 1997), hence the use of higher order terms. By inserting eq. 2 into 1 we can obtain theoretically the MRI signal intensity that is usually compared with experimental data after normalization. In many materials reported in the literature, such as hydroxypropyl celulose (HPC) hydrogels (Baumgartner et al., 2005), polyacrylamide (PAA) beads (Barros et al., 2012), or for xanthan gum hydrogels (Mikac et al., 2010), the signal intensity presents a maximum with the solid content, which depend on the imaging conditions such as the magnetic field, at φ 0.2–0.4 for the examples shown in Fig. 1. Hence, it is not uncommon in MRI images that the brightest spots do not represent zones with maximum amount of water. Because the same intensity ratio can correspond to two very different φ values, it is required for spatial quantification to know in which side of the curve each voxel is. In dynamic swelling experiments, where the location of the solvent and the initial unswollen material are known, this can be determined easily (Barros et al., 2012). However, if a MRI image is taken from a homogeneous gel of unknown concentration, it would not be possible to quantify φ without further measurements (e.g. T_2).

This simple analysis is however difficult to apply to real heterogeneous foods, such as a tomato, where the proton intensity, T_1 and T_2 depend on the location and ripening time (Musse et al., 2009). Yet, it should be expected to be applicable to simpler food-like systems, as shown for the swelling and dissolution of xanthan gum (Mikac et al., 2010). In the current work we considered heat-induced whey protein hydrogels, extensively researched in the past, due to their relevance to dairy fouling (Blanpain-Avet et al., 2016). During the removal of whey-rich fouling deposits with alkaline solutions, the protein hydrogels swell, and the extent of swelling is important to understand the dissolution rate (Saikhwan et al., 2010). Due to the relevance of swelling, there have been many studies to quantify the overall volumetric swelling degree Q from volumetric or gravimetric measurements, typically at swelling equilibrium (Li et al., 2016). However, such studies do not provide any spatial information of the local swelling degree, in particular at the gel-solvent interface where such information is highly desired to understand dissolution. Recently, we have shown that wide-field fluorescence microscopy can be used in quantification of Q for whey protein gels swelling at alkaline pH (Liu et al., 2017). Fluorescence microscopy requires labeling of solid matrix, the whey proteins in this case, which can change some of the properties of the gels made. Hence, the feasibility of dye-free MRI to quantify the water/protein content in hydrogels, particularly at alkaline pH, is one aim of this manuscript.

In fact, whey protein hydrogels have already been investigated using MRI. The swelling of whey protein gels was dynamically monitored at three different pH, recording MRI images and average T_1 and T_2 at different swelling times (Oztop et al., 2010). In order to distinguish better the gels from the aqueous solutions which where immersed, manganese chloride was used as a contrast agent. However, T_2 is strongly affected by the manganese ions concentration (Oztop et al., 2014), as in eq. (2), which makes the quantification of the water content during swelling very problematic, for example, because the Mn^{2+} can diffuse out of the gel (Oztop et al., 2010). Hence, in that initial MRI study no quantification of the water/protein content was performed. Recently, the water content of whey protein microgels has been estimated from T_2 measurements using NMR relaxometry (Peters et al., 2016), not with MRI.

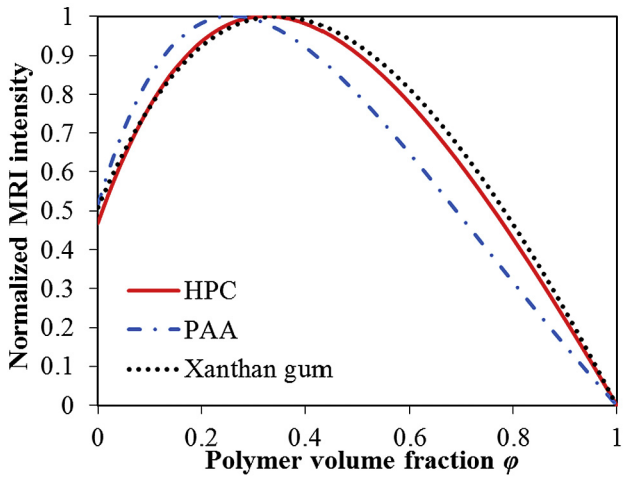

Fig. 1. Normalized MRI signal of different materials calculated using T_1 and T_2 correlations reported in the literature at different magnetic fields: HPC at 2.35 T (Baumgartner et al., 2005), PAA at 9.4 T (Barros et al., 2012), and xanthan gum at 2.35 T (Mikac et al., 2010), using eq. (1) with T_E = 20 ms and T_R = 0.5 s.

2. Materials and methods

2.1. Swelling and drying of whey protein hydrogels

Whey protein isolate (WPI) was purchased from Davisco (USA), protein content >90 wt%, of which ~65% is βLg and ~27% αLa. Most of gels were formed of 15 wt% WPI heated at 80 °C for 1 h at pH ~7; particulate gels were formed at similar conditions but with 0.15 M NaCl added. Stranded WPI gels were also formed at pH 11 heated at 50 °C for 20 min. Gels at protein concentrations between 10 and 30 wt% were made at these three gelation conditions inside centrifuge tubes. Swelling experiments at different pH (using NaOH) and [NaCl] were performed as described previously with MilliQ water (Li et al., 2016), and without additional doping agents, in order to study only homogeneous gels. Most gels were swollen to equilibrium after several days. Circular gels were cut of a thickness of ~6 mm, and a diameter of ~13 mm. Drying experiments were performed in a conventional forced convection oven at 50 °C, MRI images were taken at different drying times. The weight of hydrogels was recorded at the beginning (m_0), and during swelling and drying (m_t). Knowing the initial protein concentration of the gels (w), the protein volume fraction φ and its reciprocal, the volumetric swelling ratio Q (of the whole sample) is calculated using (Li et al., 2016):

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