Investigation of the nature of water in hydrogels and in fluff-pulp with NMR

G.S. Pell[1], M. Landeryou[1], A. Cottenden[2], R.J. Ordidge[1]

[1]*Department of Medical Physics and Bioengineering, University College London, UK;* [2]*The Incontinence Group, Department of Medical Physics and Bioengineering, University College London, London*

INTRODUCTION: The area of investigation concerns the mechanisms of water absorption in the principal constituents of incontinence pads. The absorbent layer in the pads consists principally of superabsorbent polymer (SAP) grains scattered in cellulose-based fluff-pulp. Superabsorber is a hydrogel, a swollen polymer, which is able to absorb huge quantities of fluid (up to 70 times its own weight). Its use has been suggested for tissue phantoms (1). NMR has been used to investigate water content and mobility in these substrates. T1 and T2 relaxometry have been employed in conjunction with diffusion, proton density (PD) and magnetisation transfer contrast (MTC) NMR. These techniques have enabled investigation of the *free* or *bound* state of water in these materials.

METHODS: Experiments were carried out on a 2.35T magnet interfaced to a SMIS console. The SAP used in this study was a mixture of crosslinked polyacrylic acid and sodium polyacrylate.

PD and MTC (3 expts., 42 measurements): 1g of (a) SAP, (b) fluff-pulp and (c) a mixture of 50% SAP and 50% fluff-pulp, were added to 10ml of each of the following liquids: (i) distilled water, (ii) 0.5wt% NaCl/water solution, (iii) 1% NaCl; (iv) 10% NaCl (urine is approx. 0.9wt% NaCl). Transverse, 1-D profiles of the entire volume were acquired with a standard spin-echo sequence (TR=15s; TE=30ms; 6 or 30 repeated acquisitions before and after addition of liquid) with 5s pre-pulse for MTC (power=60mG). Interleaved acquisition of PD-weighted (PD-w) (frequency offset, Δf=100kHz) and MTC spectra (Δf=2kHz).

T1/T2/ADC (4 expts.): 1g of (a) SAP and (b) fluff-pulp were added to 10ml of (i) distilled water and (ii) 10% NaCl. A similar SE sequence was employed. For T1 measurements, TR was varied in 8 steps from 0.5-5s. For T2 measurements, TE was varied in 8 steps from 30-900ms. For ADC measurements, a spin-echo sequence with bipolar diffusion gradients alternatively applied along read and phase directions was employed (Δ=44ms; δ=22ms; b=700s/mm^2). All profiles were analysed by integrating for the area.

RESULTS & DISCUSSION: PD-w and MTC data are shown in Fig. 1(a,b) and T1/T2/ADC results in Fig. 2. The MTC ratio is defined as M_s/M_0 where M_0 and M_s are the PD-w and MTC-weighted profiles respectively. The PD-w signal and MTC ratio always declined on mixing the fluid and the substrate but in varying degrees in each case (Fig. 1(a) & (b)). This indicates different degrees of water binding. The finding of only a relatively small PD decline on mixing the water and the SAP, indicates that water is not principally tightly bound by the polymer. It is presumably absorbed via driving forces such as osmotic pressure and electrostatic mechanisms through the porous structure of the hydrogel. The minimal change of the MTC ratio in SAP is a further indication of the absence of a tight water binding mechanism. It has been suggested that principal binding sites of water in SAP are electric dipoles (-COOH) or fixed charges (-COO-) of carboxyl groups (2). The resulting hydrogen bond is apparently of insufficient strength or present in insufficient numbers, for the water to be considered bound in the NMR sense. With increasing NaCl concentration, the PD and MTC changes decreased and increased respectively, but both only to a small extent. This reflects the reduced ability of hydrogels to absorb fluid in the presence of salt solutions which is due to the polyelectrolytic nature of SAP. In the fluff-pulp, the PD-w signal decreased to a far greater extent and a larger MTC effect was observed. Cellulose molecules are relatively long and flat with a large surface area that offers many hydroxyl (-OH-) binding sites to water (via H_2-bonding). The molecule offers a large interfacial area for cross-relaxation between the bulk, mobile water and the absorbed, bound component.

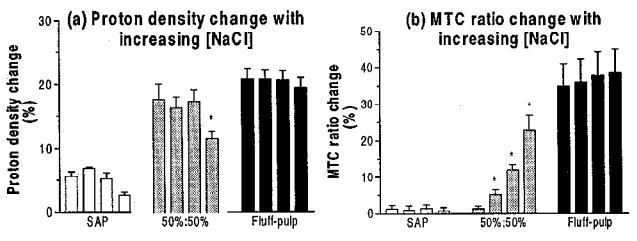

Fig. 1(a) and (b) PD-w and MTC ratio changes with increasing [NaCl] (0,0.1,1,10%). Data normalised to the control level. * indicates a significant difference with respect to the value with water ($P < 0.05$). A positive % parameter. Error bars are ±SEM.

The reduction in the T2 (Fig. 2) is sufficient to account for the PD-w signal changes (at TE=30ms). The reduction in T1/T2 reflects a decreasing water mobility associated with an increased proton correlation time, τ_c, in the liquid/sample mixture. A greater change in τ_c occurs in the more tightly bound fluff-pulp system. In the SAP mixture, the increasing τ_c is presumably simply due to a decreased water mobility as the hydrogel expands, while in the fluff-pulp, the H_2-bonded water molecules will contribute to a larger change. On changing from water to NaCl soln., the T1/T2 data does not appear to significantly change. The mechanism of absorption in the presence of a salt solution does not involve any major structural changes that would be expected to affect τ_c (and presumably reflects an osmotic response). Diffusion coefficients declined in both materials to the same degree which indicates a similar degree of restriction in translational water mobility.

CONCLUSION: This study has demonstrated the utility of using NMR to investigate the absorptive mechanism of water transport and retention in the constituent materials of incontinence pads.

REFERENCES:

(1) Gore, J.C, et al.., MRM, **9**, 325-332 (1989)

(2) Rajamohanan, P.R., et al., *Macromol.* **28**, 2533-2536 (1995)

ACKOWLEDGEMENTS: This work was carried out in the Department of Biophysics at the Institute of Child Health, UCL, London and in conjunction with the Incontinence Group of the Department of Medical Physics, UCL.

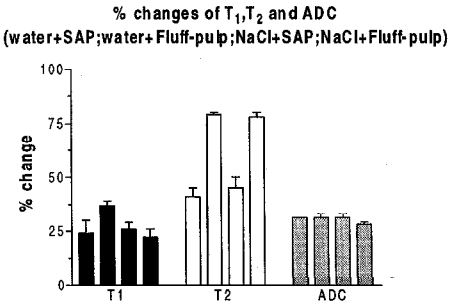

Fig. 2. Percentage change of relaxation parameters and ADC (ratio – before addition:after addition) in liquid and material combinations as indicated in the figure title. A positive percentage change indicates a decrease of the