A Solid Marker Material for MRI with Adjustable Relaxation Properties

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Introduction

To fill a fiducial marker with MR-visible material, various liquids have been used in the past such as water doped with contrast agents (e.g., Gd-DTPA), $CuSO_4$ solutions, vegetable and animal oils. Furthermore, solid or semisolid organic compounds such as agar and agarose gels, vinyl plastisol (VP), petroleum gels, have been evaluated to avoid re-filling of the markers [1, 2]. Here we compare some of these substances and describe a solid, water based substance for use in fiducial markers.

Materials and Methods

Sample Preparation

Vinyl plastisol was purchased in form of dermal pads (Spenco Chemicals, Haywards Health, West Sussex, England), and lightly cross linked poly acrylate gel (PAA) (Sigma Aldrich, Steinheim, Germany; partial sodium salt, 2% in water with 1:100 Gd-DTPA) was prepared. Hot aqueous solutions (20 grams each) of different concentrations of PVA powder (Alfa Aesar, Karlsruhe, Germany; av. mol. weight: 88000-97000, 98-99% hydrolyzed, polymerization > 1000) were prepared in plastic tubes which were afterwards cooled to room temperature. Similarly, 15 wt% solutions of PVA in water (10 grams each) were doped with different concentrations of Gd-DTPA. PVA solutions were frozen overnight at -18 °C followed by thawing at room temperature for 9 hours (freeze/ thaw cycle, FTC). The FTC process creates PVA hydro gel (PVA-H), a result of the formation of hydrogen bonds between hydroxyl groups on the PVA chains and of crystallites in the amorphous matrix of hydro gel. For each sample 7 FTCs were performed.

Relaxometry

Relaxation times were investigated at a 1.5 Tesla whole body MR system (1.5 T Magnetom Symphony, Siemens, Erlangen, Germany). T1 times were measured using a saturation recovery turbo-FLASH pulse sequence (TI = 20 ms, 30 ms, 50 ms, …, 5000 ms) and T2 times were measured using a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence (32 echoes, TR = 3000 ms, ΔTE = 15 ms and 50 ms). Spin density relative to water (ρ_{H2O}) was measured using a spin-density weighted FLASH pulse sequence (TR / TE = 5000 ms / 5.9 ms).

For the PVA-H samples with different contrast agent concentrations relaxivities r_1 and r_2 were calculated from the relaxation rates $R_1 = T1^{-1}$ and $R_2 = T2^{-1}$ assuming a linear dependency on the contrast agent concentration C:

$$R_1 = R_{1,0} + r_1 \cdot C \quad \text{and} \quad R_2 = R_{2,0} + r_2 \cdot C$$

Here, $R_{1,0}$ and $R_{2,0}$ denote the relaxation rates of the gel without contrast agent.

Results and Discussion

Table 1 summarizes ρ_{H2O}, T1, T2 and chemical shifts (values taken from literature [1]) of the materials. The relaxation properties of water can be adjusted with contrast agents, but liquids tend to leak or dry out of signal reservoirs which is also seen with PAA. VP, Vaseline, animal and plant oils have a non-vanishing chemical shift that leads to displacement artifacts which need to be avoided for markers [1]. In the commercial VP material relaxation times could not be varied, and silicon rubber has a very low relative spin density.

The relaxation times of PVA-H decrease with increase in PVA concentration (Fig. 1), however, it was observed that PVA-H samples with a PVA concentration > 20 % become inhomogeneous. In the Gd-DTPA-doped PVA-H (15 wt %), a linear increase in relaxation rate is seen (Fig. 2). The relaxivities for it were determined: $r_1 = 3.07$ ms^{-1} ($R_{1,0} = 1.1$ s^{-1}) and $r_2 = 3.07$ ms^{-1} ($R_{2,0} = 5.4$ s^{-1}).

PVA-H has high ρ_{H2O} and a sufficiently long T1 and T2 which can be shortened by adding contrast agents. Although PVA-H consists of two components, water and PVA, it shows a mono-exponential T1 and T2 relaxation [3]. With each FTC, PVA solutions get more solid, and completely solid PVA-H is formed after 7 FTCs.

Substance	ρ_{H2O} [%]	T1 [ms]	T2 [ms]	σ [ppm]
Water (1:100 Gd)	100	51	47	0.0
PVA-H (10%)	95	983	173	
PVA-H (15%)	90	899	159	
PAA (2%)	86	49	44	
Vinyl plastisol	53	147	33	2.4
Vaseline	69	87	49	3.1
Silicon rubber	5	693	20	

Table 1: ρ_{H2O}, T1, T2, and chemical shift σ of the studied substances. Chemical shift values are taken from the literature.

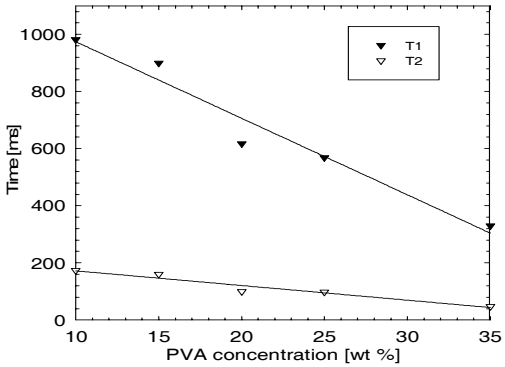

Fig. 1: Relaxation times T1 and T2 as a function of PVA concentration.

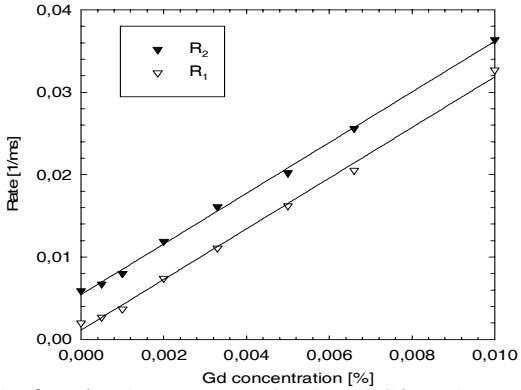

Fig. 2: Relaxation rates as a function of Gd-DTPA concentration in a 15 wt% PVA-H.

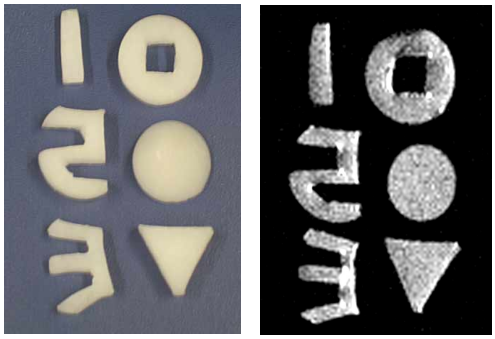

Fig. 3: Photograph (left) and MR image (right) of 15 wt% PVA-H without contrast agent.

PVA-H is a rubber like solid hydro gel which is totally non-hazardous to human body [4]. PVA-H is known to dry when exposed to air but remains stable when stored in an air-tight container. It can be cut with a knife into desired shapes (Fig. 3) which makes it an ideal material for signal reservoirs in tracking coils for MR-guided tracking coils, as localization markers in stereo-tactic surgery, for quality assurance phantoms.

References

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