Design of a fluorinated magneto-responsive material with tuneable ultrasound scattering properties

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Due to their numerous original properties, fluorinated materials are used in a wide variety of applications including coating agents for cooking devices or fabrics, ion exchange membranes or as biomaterials for cardiovascular implants. Owing to their very low solubility in water (less than 10 ppm) and, on the contrary, to their high compressibility and ability to dissolve large quantity of gases (O_2, N_2, CO_2...), volatile fluorocarbons can be used for therapeutic applications in the inner components of ultrasound contrast agents (UCA), commonly referred as "microbubbles".

The UCA echogenicity relies on the impedance contrast between the tissues mainly made of water ($Z_{water} \approx 1.5\times10^6$ Rayl) and the materials to be injected, which is often a gas phase ($Z_{air} \approx$ 340 Rayl). However gas microbubbles also have a short lifetime due to their physicochemical instability in a fluid and tend to rapidly burst or to coalesce. One way to increase the lifetime of UCA in blood is to mix air with a perfluorocarbon gas that presents a very low solubility in the aqueous phase, thus acting as "osmotic agent" to slow down the Ostwald ripening process. Several routes were developed to obtain longer-lasting UCA, on the one hand by coating the bubbles with a stabilising shell of lipids or polymers [1,2], on the other hand by adding to air or nitrogen a partial pressure of a fluorinated gas, in that case wrapped by a shell of either hydrogenated [3] or F-alkylated double-tailed phospholipids[4]. Volatile fluoroalkanes incorporated in microbubbles are octafluoropropane [5], decafluorobutane, tetradecafluorohexane (commercialised as the Fluorinert™ FC-72 reference) [3,4], or perfluorooctylbromide (PFOBr) [2]. Recently, several teams reported the decoration of the surface of microbubbles with iron oxide nanoparticles, both for pure air [6] and for mixed air/fluorocarbon gas bubbles [5,7]. The idea was to be able to guide such magnetic microbubbles against the strong flow-rate of blood circulation by the use of a magnetic field gradient.

Thus, the US imaging community is still in search for alternatives to gas bubbles, which present a high echogenicity but poor long term stability. We propose here a new type of materials made of fluorinated ferrofluid oil droplets exhibiting both a large sound-speed contrast (1/3) with aqueous solution (500 $m\cdot s^{-1}$/1500 $m\cdot s^{-1}$) and sensitivity to an external magnetic fluid. The obtained objects are not only magnetically guidable but also present the originality to exhibit strong Mie resonances at specific frequencies [8], that vary depending on the intensity and the orientation of the external magnetic field with respect to the wave propagation vector [9]. When dispersed in a yield-stress hydrogel, these droplets exhibit outstanding magnetic-responsive attenuation properties. First, we will describe the process that was used to obtain the magnetic nanoparticles dispersed in the fluorinated oil. Then, we present the fabrication of the monodisperse emulsions in a yield-stress fluid and their acoustic characterisation. These results also pave the way to the realization of tuneable acoustic metamaterials [10]

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