SOLVATO-MORPHOLOGICALLY CONTROLLED, REVERSIBLE PHOTO-ACTUATED HYDROGELS, OPERATIVE IN NEUTRAL ENVIRONMENTS.

Novelty/ Progress Claims

In this study photo-actuator hydrogels were generated using a *N*-isopropylacrylamide-co-acrylated spiropyran-co-acrylic acid (p(NIPAAM-*co*-SP-*co*-AA) copolymer, in a 100-1-5 mole ratio. Different ratios of organic solvent: water (tetrahydrofran(THF), dioxane and acetone) were used as the polymerisation solvent. Varying the volume ratio of the solvent mixtures, resulted in hydrogels with different pore sizes and therefore different extent of swelling/shrinking and actuation kinetics.

Background

In previous years, photo-responsive hydrogels reported in the literature have been synthesised by co-polymerisation of *N*-isopropylacrylamide (NIPAAM) with spiropyran (SP) derivatives. To induce re-swelling of the hydrogels external protonation is required, typically done by immersing the hydrogel in strongly acidic environments[1-3]. Moreover, re-swelling times are long, typically up to several hours. These disadvantages have restricted the use of photo-actuated hydrogels to applications that employ single-use methods.

Recently, acrylic acid (AA) has been incorporated as an internal source of protons, removing the requirement of external acidic environments.[4] In water, the AA comonomer dissociates, resulting in the protonation of the photochromic SP to protonated merocyanine ($MC\text{-}H^+$). This form is hydrophilic, allowing the hydrogel to swell. Exposure to white light promotes isomerisation of the $MC\text{-}H^+$ form to the hydrophobic SP form, which triggers contraction of the hydrogel. (*Figure 1*)

The polymerisation solvent has been shown to directly influence the morphology of the hydrogel, by producing porous hydrogels of different pore sizes[5]. This has an impact on the diffusion path length for water molecules moving in/out of the hydrogel matrix, thus improving the swelling and shrinking kinetics of the hydrogel[6].

Description of the New Method or System

Three different organic solvents were used in ratios with Deionised water, THF, Dioxane and Acetone. The aim was to study the effect the different solvents have on the morphology of the hydrogel. The hydrogels were photo-polymerised using photo-masks resulting in freestanding hydrogel discs. Using a digital microscope the shrinking and re-swelling mechanism was studied under white light irradiation and in the dark, respectively (Figure 2 and 3).

Using this method the hydrogels were shown to successfully repeatable (figure 3b). In the aim to understand the morphology, A SEM study was carried out of each hydrogels (figure 4). A rheology study was carried out; studying the effect the different solvents have on the curing times (figure 5).

Experimental Results

By alternating the solvents and ratios in the polymerisation solvent, a remarkable contraction in hydrogel size of up to 45% of its fully hydrated size after four minutes of white light irradiation was obtained. The hydrogel re-swelled to ~85% of its fully hydrated size after 11 minutes in the dark. This represents, to our best knowledge, the greatest reversible photo-induced size change of a hydrogel in the absence of any other stimuli (Figure 2+3).

The result from the SEM study has resulted in different pore sizes dependent on the solvent/ratio used as the polymerisation solvent (Figure 4). The SEM micrographs have demonstrated, with increasing organic solvent incorporated into the polymerisation solvent the more uniform the hydrogels pores become. The pores in hydrogels with less organic solvent incorporated are more varied in size and are less uniform.

The curing study has provided the information of how the different polymerisation solvents change the curing time required to successfully polymerise each hydrogel. With increasing organic solvent incorporated in the polymerisation solvent ratio the longer the polymerisation time becomes. (Figure 5)

In the same ratio dioxane has shown to take the longest time to polymerise when compared to THF and Acetone this can be reflected in the SEM micrograph results.

This study has been successful in demonstrating the effect different solvents have on the morphology of these hydrogels.

Word Count: 598/600

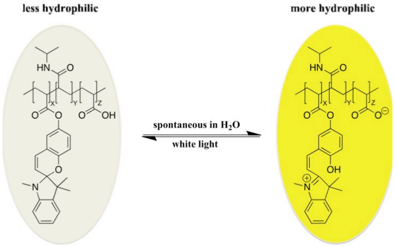

Figure 1. Self-protonation of p(NIPAAm-co-SP-co-AA) hydrogels in a neutral aqueous solution.

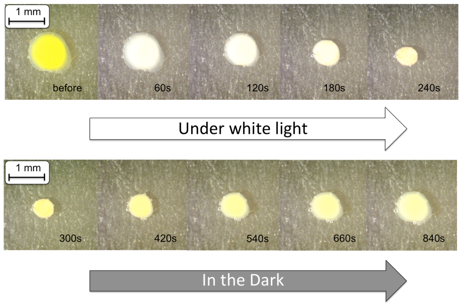

Figure 2. Microscopy images of hydrogels microstructures during one shrinking and re-swelling cycle under white light and in the dark, respectively.

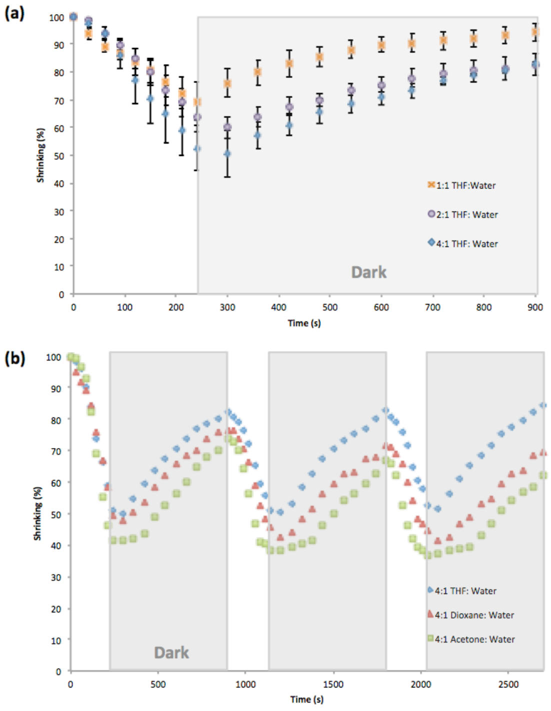

Figure 3. Shrinking (under white light) and re-swelling (in the dark) (a) a single cycle of 3 ratios of THF: water as the polymerisation solvent, (b) demonstrating the affect different solvents have on the repeatability of these hydrogels.

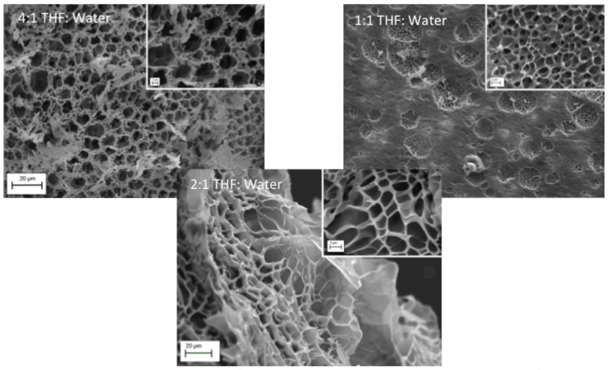

Figure 4. SEM Images demonstrating pores sizes relying on the polymerisation solvent.

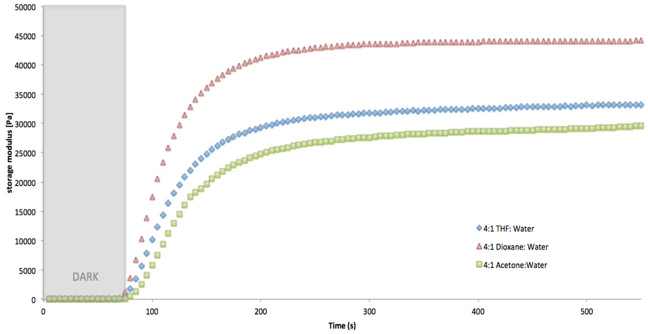

Figure 5. Rheology demonstrating the different curing times due to the solvent dependency. White light curing was initiated after 60 seconds.

REFERENCES:

1. S. Taku, S. Kimio, T. Toshiyuki and K. Toshiyuki, *Soft Matter*, 2011, **7**.
2. K. Sumaru, K. Ohi, T. Takagi, T. Kanamori and T. Shinbo, *Langmuir : the ACS journal of surfaces and colloids*, 2006, **22**, 4353-4356.
3. T. Satoh, K. Sumaru, T. Takagi, K. Takai and T. Kanamori, *Physical chemistry chemical physics : PCCP*, 2011, **13**, 7322-7329.
4. Z. Bartosz, F. Larisa, T. Jannick, B.-L. Fernando and D. Dermot, *Soft Matter*, 2013, **9**.
5. X. Zhang, R. Zhuo and Y. Yang, *Biomaterials*, 2002.
6. Z. Xian-Zheng, Y. Yi-Yan and C. Tai-Shung, *Langmuir*, 2002, **18**.