TUNING THE RHEOLOGY OF HYDROPHOBIC MATERIALS IN AQUEOUS SYSTEMS USING RESPONSIVE SURFACTANTS

Emma Jones,[1,2,3], Esther García-Tuñón[2,3]
[1]*Leverhulme Research Centre for Functional Materials Design, University of Liverpool, L7 3NY*
[2]*Materials Innovation Factory, University of Liverpool, L7 3NY*
[3]*School of Engineering, University of Liverpool, L69 3GH*
sgejone4@liverpool.ac.uk; egarciat@liverpool.ac.uk

Robocasting is an additive manufacturing technique whereby formulations are extruded through a fine nozzle to create self-supporting 3D structures. To ensure successful printing, said formulations must display specific rheological behaviours that depend on the application. The printability of soft materials can be quantitatively described with relatively simple oscillatory tests in a rotational rheometer using three parameters: the stiffness of the network at rest (G_{LVR}'), the solid-to-liquid transition point, σ_f, and the flow transition index, which relates the flow and yield stresses ($FTI = \sigma_f/\sigma_y$).[1]

Printable formulations of ceramics and 2D materials incorporating a variety of rheological modifiers are well known.[2,3] One such modifier, known as branched co-polymer surfactant (BCS, $PEGMA_5/MAA_{95}$-$EGDMA_{10}$-DDT_{10}), displays intrinsic pH responsiveness due to the incorporation of MAA monomers. Below the pKa of MAA, hydrogen bonds form between neighbouring groups - a pseudo-gel is formed, and the structure transitions to a shear-thinning, viscoelastic solid.[4] Conversely, aqueous formulations comprised of hydrophobic compounds remain poorly investigated due the difficulty in finding appropriate modifiers.

Herein, we present preliminary results on the use of BCS as a modifier for hydrophobic materials using charcoal as a standard. Initial studies have shown that BCS is an ineffective additive and requires optimisation – sedimentation was observed in all formulations tested, regardless of BCS wt/v%, while foaming in solutions with more than 2 wt/v% BCS suggests that BCS is not well adhered to the charcoal. Furthermore, said formulations never reach the "printability threshold" where the G_{LVR}' exceeds 10 kPa under any of the conditions tested. Thus, we also detail the synthesis of BCS derivatives incorporating other chain transfer agents like benzyl mercaptan and naphthalenethiol, which we predict will stabilise charcoal more effectively via additional π-π stacking interactions, the effect of which will be evident in the G_{LVR}', the σ_f and the FTI.

1 A. Corker, H. C. H. Ng, R. J. Poole and E. García-Tuñón, *Soft Matter*, 2019, **15**, 1444–1456.

2 E. García-Tuñón, G. C. Machado, M. Schneider, S. Barg, R. V. Bell and E. Saiz, *J. Eur. Ceram. Soc.*, 2017, **37**, 199–211.

3 E. Feilden, C. Ferraro, Q. Zhang, E. García-Tuñón, E. D'Elia, F. Giuliani, L. Vandeperre and E. Saiz, *Sci. Rep.*, 2017, **7**, 1–9.

4 J. V. M. Weaver, S. P. Rannard and A. I. Cooper, *Angew. Chemie*, 2009, **121**, 2165–2168.

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