scCO$_2$ AS A ROUTE TOWARDS NEW FUNCTIONAL MATERIALS

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Supercritical carbon dioxide (scCO$_2$) is a clean, cheap, non-flammable and versatile medium, ideal for the synthesis and processing of polymeric materials. In this paper we present some of the latest results obtained at Nottingham. In more detail, the synthesis of polymeric particles with controlled internal nanostructure, the enzymatic synthesis of functional polyesters starting from renewable sources and the preparation of cross-linked polymeric networks are described. All these materials have a wide range of potential applications; from engineering materials, to coatings, absorbents and for use in medical applications.

I.   SYNTHESIS OF POLYMER PARTICLES WITH CONTROLLED NANOSTRUCTURE

We have developed significant interest in the synthesis of nanostructured polymer microparticles [1, 2]. These are polymer particles featuring an array of internal ordered structures which could find utility for applications such as impact modifiers, fillers, photonic crystals, solar cells and data storage.

We have demonstrated that reversible addition-fragmentation chain transfer (RAFT)-controlled polymerisations in CO$_2$ show high control over blocking efficiency. By carefully choosing the monomer types, different internal morphologies could be obtained. This is a direct result of the phase separation given by polymer blocks with different chemical properties (*e.g.* hydrophilic/hydrophobic *etc*). The bond between the two blocks prevents macroscopic phase separation, and so the dimensions of the polymer chains result instead in formation of separated nanoscale domains.

Figure 1 shows the one-pot method exploited for the clean preparation of nanostructured polymer microparticles in scCO$_2$.
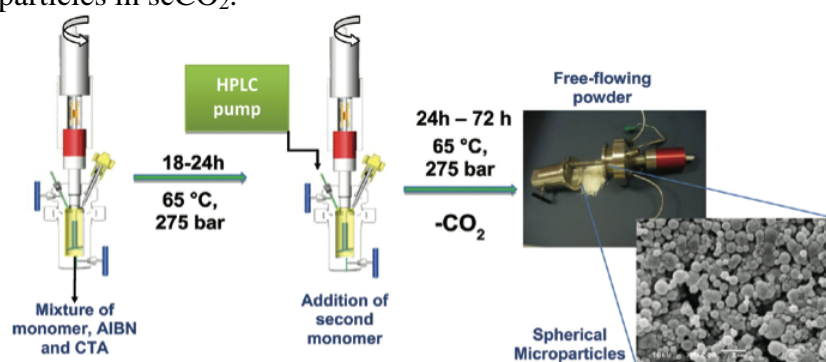
Figure 1: One-pot method for the preparation of polymer microparticles in scCO$_2$.

A wide range of monomer types, such as methacrylates, acrylamides and styrenics have been successfully used to obtain block copolymers with phase separation at the nanoscale level. Transmission Electron Microscopy (TEM) analyses showed that the particular nanostructure can be tuned by varying the volume fractions of the two blocks (Figure 2).
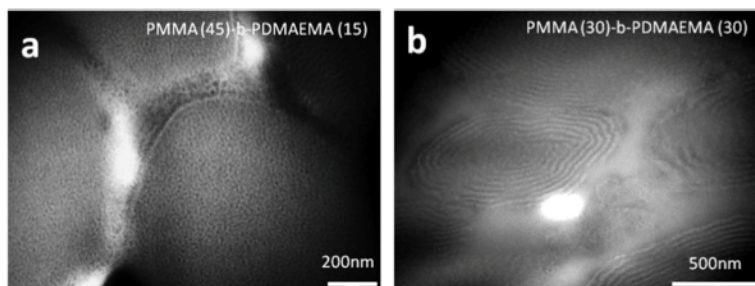
Figure 2: TEM images of two poly(methyl methacrylate)-*b*-poly(N,N-dimethylaminoethyl methacrylate) copolymers with different volume fractions (chain lengths) of the two blocks leading to completely different polymer morphologies; (a) spherical domains, (b) lamellar domains

II. LIPASE CATALYSED SYNTHESIS OF RENEWABE POLYESTERS IN scCO2

In the last few years, the use of renewable natural monomers became one of the most important topics in modern polymer science. Several sources ranging from trees, plants and algae have been exploited to extract from them the monomer materials required to prepare novel renewable polymers [3-6]. Among these, the outer birch bark is becoming a more and more important source of renewable molecules and monomers [5, 7, 8].

About 40% of dry birch bark is composed of suberin: a macromolecular network consisting of cross-linked aliphatic and aromatic molecules, which can be deconstructed to obtain long carbon chain monomers with varying structures [4-6, 9].

The most abundant monomer is the *cis-9,10-epoxy-18-hydroxyoctadecanoic acid* (Epoxy Fatty Acid, EFA), which can be polymerised giving a polyester with epoxy functionalities (Figure 3).
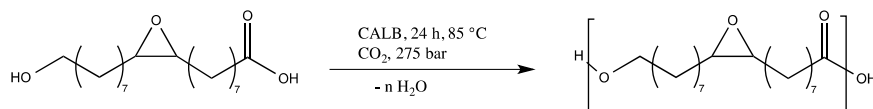

Figure 3: Synthesis of pEFA using Novozym 435 in $scCO_2$.

The two reactive end groups give us the possibility of preparing polyesters by polycondensations, but the problems of high viscosity and side reactions arise when working in bulk. This can in principle be solved by introducing a solvent, such as toluene. However, high molecular weights (MWs) are difficult to achieve even after 24 hours in conventional solvents [7].

We investigated the polymerisation of this monomer in $scCO_2$ to determine whether it is possible to prepare higher molecular weights, use shorter reactions times and also preserve the epoxy group functionality by using CO_2 as a reaction medium.

The reaction in toluene proceeded smoothly up to the end of the experiment, while the reaction in bulk showed problems due to the high viscosity (the stirrer stopped moving after 4 h). In addition to this, the product obtained in bulk was mostly insoluble in conventional solvent because of the existence of cross-linking reaction caused by the high viscosity of the bulk reaction medium. The only soluble part was characterised by low molecular weights (see Figure 4). By contrast, the product obtained in CO_2 at the same temperature was almost completely soluble and characterised by high mass average molecular weight (M_w). Thus, showing that the epoxy rings are intact (results confirmed through ^{1}H-NMR) and the polymerisation can be pushed to higher MWs by using CO_2.

Figure 4 summarises the kinetic results of the polymerisation reactions carried out in the different media.
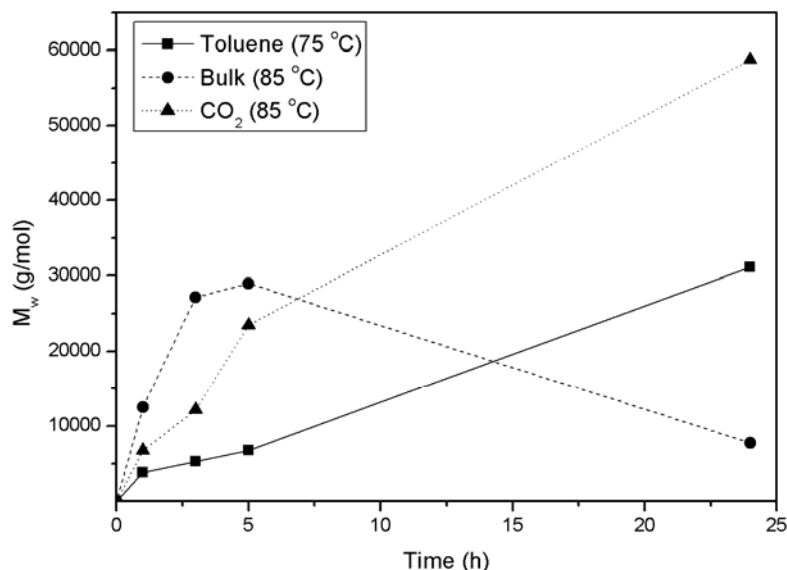
Figure 4: Mass average molecular weights (M_w) of the polymers synthesised in: toluene at 75 °C, bulk at 85 °C and $scCO_2$ at 85 °C and 275 bar.

The data in figure 4 show that carrying out the reaction in CO_2, it is possible to exploit the plasticising effects to synthesise polymers with higher M_w whilst keeping intact the epoxy functionalities. Therefore, hindering side reactions and shortening the overall reaction time.

III. Cross-linked Polymers in Supercritical CO_2

Synthesis and control of linear homo- or copolymers in $scCO_2$ is a relatively well established field [10-14], whilst the synthesis of more complex materials such as cross-linked polymers is less well explored. This may be in part be due to the difficulties related to measuring molecular weight, meaning most studies are limited to measurements of morphology, mechanical and rheological properties. $ScCO_2$ itself is a very complicated medium to understand, unlike typical solvents, the density of CO_2 above the critical pressure and temperature is highly tuneable [15] The ultimate effect this has on the cross-linking of polymers has yet to be fully researched [16]. One example of these cross-linked polymer systems is poly(acrylic acid) (PAA).

Cross-linked PAA has long been employed for its highly water absorbent properties. In order to reduce toxicity of these polymers, efforts have been made to change the solvents used. Initially benzene [17] was used, however in recent patents ethyl acetate has been proposed [18]. Whilst this progression is towards a cleaner end product, removal of the ethyl acetate is still required and we have investigated use of $scCO_2$ as an alternative with the idea that a clean, dry and pure product can be separated easily from the gaseous CO_2 upon depressurisation.

The precipitation polymerisation of PAA in $scCO_2$ has been studied for many years in batch [19] and continuous processes [20]. Desimone *et al.* have investigated the effect of cross-

linker concentration on the polymer properties and morphology [21], computationally modelled the kinetics of the precipitated polymer phase [22], and showed how the operating conditions of the continuous method affect the morphology [23], Xu *et al.* also investigated the effect of co-solvents on the molecular weight and properties of PAA [24, 25].
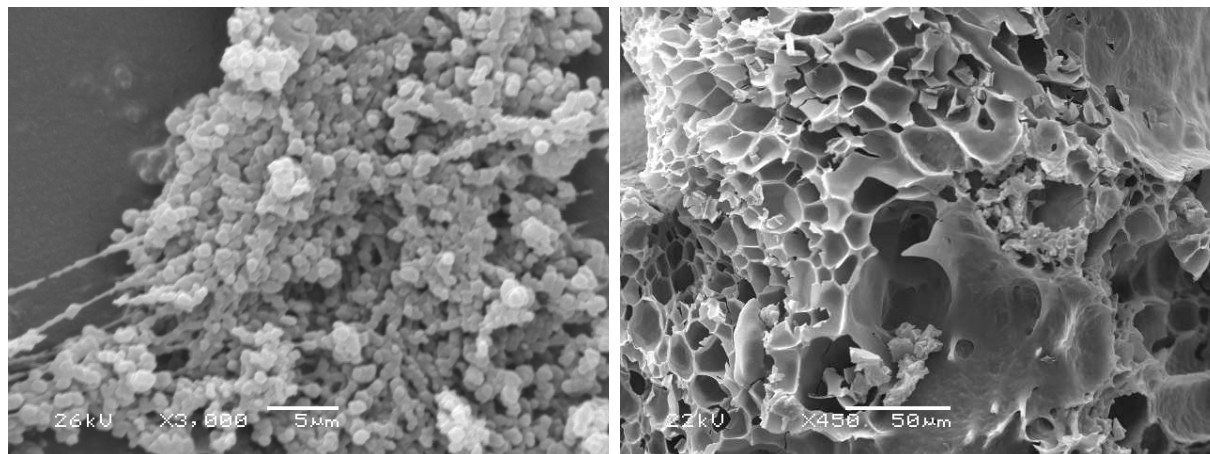
Figure 5: Scanning electron microscopy images demonstrating the synthetic temperature effect on the morphology of cross-linked poly(acrylic acid) (left) 65 °C, (right) 90 °C

Recently we have investigated the feasibility of producing commercially applicable absorbent polymers using $scCO_2$. The focus of this project was to explore the effect of the CO_2 medium on the morphology and rheological properties of cross-linked PAA. One of the immediate observations was that different conditions led to vastly different morphologies of the polymer products (Figure 5). At the lower temperature of 65 °C the polymer precipitates out of the supercritical medium as particles. However, at the higher temperature of 90 °C the polymer agglomerates becauseit is above its glass transition temperature (Tg). Although control over the morphology is not maintained, a glassy powder product is still observed.

Further investigation of these conditions can lead to a better understanding of the crosslinked polymer properties and morphologies that are created at different temperatures and pressures and hence different densities of CO_2. Simple methods such as swell tests [26, 27] and mechanical tests [28, 29] have yielded valuable data to tune the conditions of the reaction. Better understanding of the kinetics, solubility in $scCO_2$, and the way in which CO_2 affects the properties of the polymer are all required in order to move towards a commercial process.

CONCLUSIONS

$ScCO_2$ is a green and versatile alternative solvent for polymer synthesis and processing. In addition to reducing the amount of toxic volatile organic solvents $scCO_2$ can lead to completely new nanostructured polymeric microparticles and new suberin-derived polyesters with high MW which, up till now, have not been achieved using conventional techniques and solvents. In the first case the use of CO2 gives the possibility of using a green solvent-free one-pot procedure, in the second high MW polymer chains could be synthesised in shorter times whilst avoiding cross-linking side reactions.

REFERENCES

[1] J. Jennings, M. Beija, A.P. Richez, S.D. Cooper, P.E. Mignot, K.J. Thurecht, K.S. Jack, S.M. Howdle, J Am Chem Soc, 134, **2012**, p. 4772

[2] J. Jennings, M. Beija, J.T. Kennon, H. Willcock, R.K. O'Reilly, S. Rimmer, S.M. Howdle, Macromolecules, 46, **2013**, p. 6843

[3] A. Gandini, Macromolecules, 41, **2008**, p. 9491

[4] N. Cordeiro, N.M. Belgacem, A. Gandini, C. Pascoal Neto, Bioresource Technology, 63, **1998**, p. 153

[5] A. Gandini, C. Pascoal Neto, A.J.D. Silvestre, Progress in Polymer Science, 31, **2006**, p. 878

[6] P.C.R.O. Pinto, A.F. Sousa, A.J.D. Silvestre, C.P. Neto, A. Gandini, C. Eckerman, B. Holmbom, Industrial Crops and Products, 29, **2009**, p. 126

[7] A. Olsson, L. Mikael, I. Tommy, Biomacromolecules, 8, **2007**, p. 757

[8] T. Iversen, H. Nilsson, A. Olsson, Patent,*"A method for separating from suberin and/or cutin containing plants, a solid and/or oil fraction enriched in cis-9,10-epoxy-18-hydroxyoctadecanoic acid"*, **2010**

[9] R. Ekman, Holzforschung, 37, **1983**, p. 205

[10] J.L. Kendall, D.A. Canelas, J.L. Young, J.M. DeSimone, Chemical Reviews, 99, **1999**, p. 543

[11] J. Jennings, M. Beija, A.P. Richez, S.D. Cooper, P.E. Mignot, K.J. Thurecht, K.S. Jack, S.M. Howdle, J Am Chem Soc, 134, **2012**, p. 4772

[12] J. Jennings, M. Beija, J.T. Kennon, H. Willcock, R.K. O'Reilly, S. Rimmer, S.M. Howdle, Macromolecules, 46, **2013**, p. 6843

[13] G. Jaramillo-Soto, E. Vivaldo-Lima, Australian Journal of Chemistry, 65, **2012**, p. 1177

[14] H. Minami, A. Tanaka, Y. Kagawa, M. Okubo, Journal of Polymer Science Part a-Polymer Chemistry, 50, **2012**, p. 2578

[15] M. McHugh, A., V. Krukonis, J., Supercritical Fluid Extraction: Principles and Practice, 2nd ed., Butterworth-Heinemann, Stoneham, 1993.

[16] I.A. Quintero-Ortega, E. Vivaldo-Lima, G. Luna-Barcenas, J.F.J. Alvarado, J.F. Louvier-Hernandez, I.C. Sanchez, Industrial & Engineering Chemistry Research, 44, **2005**, p. 2823

[17] H. Koenig, Union Carbide Corporation, US patent, 1981, pp. 4268641.

[18] E. Sehm, The BF Goodrich Company, US, 1992.

[19] T.J. Romack, E.E. Maury, J.M. Desimone, Macromolecules, 28, **1995**, p. 912

[20] P.A. Charpentier, J.M. DeSimone, G.W. Roberts, Clean Solvents: Alternative Media for Chemical Reactions and Processing, 819, **2002**, p. 113

[21] T. Liu, J.M. DeSimone, G.W. Roberts, Polymer, 47, **2006**, p. 4276
[22] T. Liu, J.M. DeSimone, G.W. Roberts, Chemical Engineering Science, 61, **2006**, p. 3129
[23] T. Liu, P. Garner, J.M. DeSimone, G.W. Roberts, G.D. Bothun, Macromolecules, 39, **2006**, p. 6489
[24] Q. Xu, B.X. Han, H.K. Yan, Polymer, 42, **2001**, p. 1369
[25] Q. Xu, B.X. Han, H. Yan, Journal of Applied Polymer Science, 88, **2003**, p. 1876
[26] F. Horkay, D.H. Craig, Polymer Bulletin, 41, **1998**, p. 231
[27] W.F. Lee, P.L. Yeh, Journal of Applied Polymer Science, 66, **1997**, p. 499
[28] J. Aalaie, M. Youssefi, Journal of Macromolecular Science Part B-Physics, 51, **2012**, p. 1027
[29] H. Sheikhy, M. Shahidzadeh, B. Ramezanzadeh, F. Noroozi, Journal of Industrial and Engineering Chemistry, 19, **2013**, p. 1949