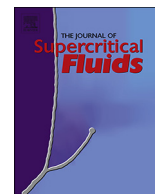




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Synthesis and control of crosslinked poly(acrylic acid) based viscosity modifiers using dense phase carbon dioxide as a solvent

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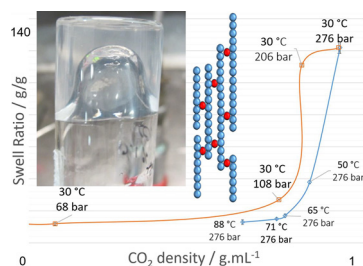
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GRAPHICAL ABSTRACT

Supercritical CO₂ provides a versatile and clean solvent system for preparation of poly(acrylic acid) gels and super-absorbents. Careful control of scCO₂ density can strongly influence the density of cross links in the gel material leading to control of key materials properties.



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ABSTRACT

We investigate the clean synthesis of a cross-linked poly(acrylic acid) viscosity modifier using supercritical CO₂ to replace more hazardous volatile organic solvents that are typically used for this process. The polymers were analysed by aqueous swell ratio studies to demonstrate the effect of process conditions such as pressure and temperature on the cross-link density of the materials. The reactions were optimised to yield high swelling polymers of up to 134 g water/g polymer. Dynamic mechanical analysis (DMA) was also applied to investigate the mechanical properties of the synthesised cross-linked poly(acrylic acid) materials and these data were directly correlated with swell ratio. In addition, rheological studies demonstrate that the hydrated gels are comparable with commercially available equivalents.

1. Introduction

Cross-linked poly(acrylic acid) (PAA), otherwise known as a carbomer, is a material commonly used as a superabsorbent polymer, or a thickener for cosmetic products. Conventionally, carbomers are produced *via* precipitation polymerisation using solvents such as benzene [1,2], DCM [3], or more recently co-solvent combinations of ethyl acetate and hexanes [4]. Significant efforts have been focussed upon the

use of less toxic solvents largely because of the regulatory requirements in personal care and cosmetics and also because complete removal of residues is highly energy intensive.

Supercritical CO₂ (scCO₂) has shown promise as an alternative to volatile organic solvents for polymerisations and polymer processing [5–12]. Indeed, several studies have investigated the use of scCO₂ for the polymerisation of acrylic acid (AA) to produce cross-linked PAA without the use of VOCs. One of the first examples was a BASF patent

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filed in 1987 [13], which demonstrated that Poly(acrylic acid-co-methacrylic acid) viscosity modifiers (viscosity max ~ 26 Pas, spindle rpm 5.5, pH 8) can be produced from scCO_2 at temperatures of 60–110 °C and pressures of 120–200 bar. In 1995 Romack et al. investigated polymerising AA through this approach, setting a fixed temperature of 65 °C, whilst varying the pressure from 165 to 345 bar, but noting no effect on molecular weight, dispersity, particle size or morphology [14]. Further studies conducted by Tao et al. demonstrated the synthesis of cross-linked PAA in scCO_2 at 50 °C, before then scaling up to a promising semi-continuous process at 70 °C [15]. Rheological experiments on hydrated PAA gels demonstrated a thickening effect (viscosity from 100 Pas at 0.01 s^{-1} to 0.1 Pas at 100 s^{-1}), but without evidence of commercial applicability. Under certain conditions there was significant formation of PAA coagulum that could not be dispersed in water and hence did not contribute to increasing the viscosity of the aqueous PAA dispersions. A model of particle formation of PAA in the polymerisation was proposed suggesting that control of molecular weight and reaction temperature played an important role in determining PAA particle size and suggesting that agglomeration of such particles prevents dispersion [16].

There is a dearth of publications exploring the effects of scCO_2 reaction conditions on the resulting cross-link density. In this paper, we explore these parameters and also the effect upon the swelling properties of these materials. We also demonstrate that scCO_2 can be used to minimise monomer residues to provide a dry, monomer free polymer powder.

2. Experimental

2.1. Materials

CO_2 (99.99, SFC grade) was obtained from BOC gases, glacial acrylic acid (AA) (99.9%, MEHQ – 200 ppm) was obtained from VWR chemicals. Pentaerythritol triallyl ether (tech. 70% tri-functional), 1,1'-Azobis(cyclohexane-1-carbonitrile) (V-88) and 2,2'-Azobis(2-methylpropionitrile) (AIBN) were obtained from Sigma Aldrich. 2,2'-Azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70) was obtained from Wako chemicals. All chemicals were used as received.

2.2. Synthesis of PAA

A solution of AA (15 mL, 208 mmol) and pentaerythritol triallyl ether (PETAE) (0.15 mL, 0.701 mmol) was prepared and flushed through a purge line. V-70 (0.112 g, 0.365 mmol) was placed into the reactor with a flow of CO_2 (inlet pressure ~ 2 bar) through the access hole for 30 min to remove oxygen. The reactor was then sealed, the pressure was raised to 175 bar, and temperature was raised to 30 °C. The pre-prepared monomer solution (6 mL) was injected into the reactor via the addition line and an HPLC pump at 3 mL/min (1 mL excess allowed for volume of the line). The addition line was then closed and the reactor topped up to the required pressure with scCO_2 .

The conditions were maintained for 18 h before turning off the heater and allowing the reactor to cool to below 25 °C, at which point the exit tap was opened slowly to vent the reactor. A low bulk density powder was collected and yields were measured gravimetrically to be between 40 and 99%.

2.3. Swell test

Swell tests were performed in triplicate by measuring polymer sample (0.05 g) inside a closed drawstring tea bag (unknown mesh size), before being immersed in de-ionised water at room temperature. Gravimetric measurements were taken daily after hanging for 15 min to allow surface water to drip off. Measurements were carried out until an equilibrium had been reached.

2.4. DMA

Dynamic mechanical analysis using a TT DMA (Mettler Toledo, formerly Triton Technology) was performed on polymer bars moulded at 150 °C, in a specially constructed mould (detailed in supporting info). The samples were run in tension mode with a pre-load force of 1.5 N, and a displacement amplitude of ± 0.02 nm. The storage modulus, E' was determined at 1 Hz after a 30-min isotherm at 150 °C.

2.5. Extraction

CO_2 prepared PAA (0.5 g) was placed into a sealed mesh cage, which was positioned into a scCO_2 flushing rig (detailed in previous papers) [17]. The autoclave pressure was raised to 276 bar at room temperature (~ 18 °C) and held for 30 min to equilibrate the system and allow AA to diffuse into the scCO_2 . Flushing was conducted by opening the inlet and outlet valves of the autoclave simultaneously to provide a constant flow of scCO_2 . After 140 min, the flushing was stopped by closing the inlet valve and allowing the autoclave to vent to ambient pressure. The cage was opened, the PAA powder collected and mass loss measured gravimetrically. The experiment was conducted each time with fresh powder, and for each separate time-period the flushing was maintained continuously.

Residual AA was measured by high performance liquid chromatography (HPLC). PAA (0.1 g) was gradually added to 18 mL of HPLC water and stirred into solution for 10 mins. Once the material was wetted, 10% NaCl (0.5 mL) was added to the solution followed by 10% NaOH (0.5 mL). The solution was stirred for 10 mins, then 10% H_3PO_4 (2 mL) was added. After stirring, 2 mL of 10% H_3PO_4 was added to the solution, which was stirred then filtered through a $0.45 \mu\text{m}$ filter and analysed by HPLC.

Recovery was determined by adding a known amount of acrylic acid to the solution prior to precipitation. The precipitation was performed and the extract measure to ensure acrylic acid was not also removed from the solution.

3. Results and discussion

ScCO_2 is a highly tuneable solvent, and small changes in temperature and pressure can produce significant changes in fluid density [18] which could affect the cross-link density of the PAA. To follow these changes, we initially focussed upon the very simple measurement of water absorption and swell ratio; a technique that has been used very widely to give an indication of cross-link density [19–21].

We performed a series of PAA syntheses in CO_2 with temperatures ranging from 30 °C (liquid CO_2) to 88 °C (scCO_2) at a pressure of 276 bar giving a range of CO_2 densities (0.67 g mL^{-1} to 0.94 g mL^{-1}) [22]. A tri-functional cross-linker, PETAE was chosen as a well understood and commercially utilised crosslinker. PETAE was used at constant concentration (0.27 mol% wrt. AA). Additionally, in order to maintain consistent radical flux over the temperature range, three different initiators were used. V-70 at 30 °C (half-life $\sim 10 \text{ h}^{-1}$), AIBN at 50 °C (68 h^{-1}) and 65 °C (10 h^{-1}), and V-88 at 71 °C (68 h^{-1}) and 88 °C (10 h^{-1}) (Fig. 1).

Initial experiments favoured lower temperatures (greater CO_2 density) for producing higher swelling polymers, with the highest swell ratio (122 g/g) observed at 30 °C and the lowest (11 g/g) at 71 °C. These results indicated that the CO_2 density dramatically affected the cross-link density of our materials. To explore this relationship further, the reaction temperature was fixed at 30 °C and the pressure was varied from 68 to 276 bar, to give CO_2 densities from 0.16 g mL^{-1} to 0.94 g mL^{-1} (NIST) (Fig. 2).

The maximum swell ratios were observed at the highest CO_2 pressures, and these dropped off quickly from $> 100 \text{ g/g}$ to $\sim 25 \text{ g/g}$ at reaction pressures of around 100 bar. As demonstrated in the plot, this decrease mirrors the rapid reduction in CO_2 density. It is likely that

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