POLY (ε- CAPROLACTONE) PROCESSED WITH THE RESS TECHNIQUE

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INTRODUCTION

In the present work, Rapid Expansion of Supercritical Solutions (RESS) has been used to prepare particles of two different polymers; poly(ε- caprolactone) (PCL) and a co-polymer of two different molecular weights. With the RESS technique it is possible to produce particles using a supercritical fluid as a solvent, and the particles are formed when the mixture is expanded through a nozzle [1]. Supercritical carbon dioxide (SC-CO_2) is a weak, commonly used, solvent for low molecular weight polymers, fluoropolymers and silicones [2]. One limitation when processing polymers in SC-CO_2 with the RESS technique is to find polymers that are soluble in the SC-CO_2. One way to increase the solubility of the polymer is to use a co-solvent in the process [3]. Another strategy is to work with polymers that have structures facilitating interactions with the CO_2. Kazarian et al. [4] showed that some polymers, for example PMMA and PVAc, which have carbonyl groups in the side chains interact favourably with CO_2 via a Lewis acid- Lewis base interaction. Rindfleisch et al. [5] concluded in their study that the polymer free volume is important for the solubility of a polymer in CO_2, meaning that flexible polymers chains are favourable.

In the present work, the solubility of selected polymers in SC-CO_2 respectively in a mixture of SC-CO_2 and acetone at two different temperatures was initially studied. In these investigations a supercritical fluid extraction unit was used, in which a constant flow of solvent was applied through the vessel. The solubility was determined by comparing the extracted amount of polymer with the amount of material initially placed in the vessel, per unit volume of solvent. Finally, the polymers were processed by RESS with the aim to create a superhydrophobic surface coating.

High contact angles (>150°) and low contact angle hysteresis (<5°) are needed to obtain superhydrophobic properties on a surface. To achieve these high apparent contact angles it is also necessary to tailor the surfaces with a high roughness, both on the micro and nano-scale [6]. The superhydrophobic surfaces possess self-cleaning properties, which means that a water droplet will roll off the surface instead of sliding [7]. In the present work, the surface properties were evaluated by measuring the advancing contact angle of a water droplet placed on the treated surfaces. Morphology and particle size of the coating were studied with the aid of scanning electron microscopy (SEM).

MATERIALS AND METHODS

The polymers used in the study were poly(ε- caprolactone), PCL (Mn= 10 000 g/mol) purchased from Sigma Aldrich and a random co-polymer of two different molecular weights (polymer A≈10 000 g/mol and polymer B≈ 20 000 g/mol) that have been designed and synthesised to be soluble in SC-CO_2. Ultra pure carbon dioxide (99,9 %) purchased from Air Products and acetone of 99,8 % purity form Honeywell, B&J was used.

A Supercritical Fluid Extraction (SFX™ 2-10, ISCO, USA) unit has been used for the dynamic solubility study and for spraying the polymers to coat surfaces. Stainless steel extraction vessels of 10 mL were first packed with 3,0 mm diameter glass beads and then ca 50 mg polymer was added to the vessel. Two pumps (syringe pump, model 260 D, ISCO, USA) were used to pressurise the carbon dioxide and the acetone. The vessel was first placed in the extraction unit and left for 15 minutes to achieve a stable temperature (40 or 65 degrees). The restrictor (ISCO, USA) was maintained at 70 degrees to prevent precipitation of the polymer. The pressure of 300 bars was constant during the experiments and the amount of co-solvent was ca 10 vol% of the CO_2 flow. In the case of the solubility study, the products were collected in glass vials. During the spraying of polymers, a flow of nitrogen gas was added to remove the co-solvent in the spraying jet and the surface substrate was silica plates.

RESULTS

Dynamic solubility study

In the dynamic solubility study, the polymers were extracted with a continuous flow of SC-CO_2 at 300 bars during 40 min. The effect of acetone as a co-solvent in the process at two temperatures (40°C and 65°C) was examined. Each experiment was repeated three times and the solubility values showed are a mean value from these tests. All three examined polymers show the lowest solubility at 65°C with only SC-CO_2. The solubility of PCL improved with acetone as co-solvent for both temperatures; 0,107 g/L at 40°C and 0,119 g/L at 65°C. The polymer A had the highest solubility at 40°C both with and without acetone (0,549 and 0,535 g/L). The highest solubility of polymer B was 0,394 g/L at 40°C with acetone. When comparing these three polymers, PCL has the lowest solubility and polymer A has the highest solubility value. The solubility of these polymers seems to be dependent on the density of the CO_2 since it is higher at 40°C (910 kg/m^3) compared to 65°C (809 kg/m^3) at 300 bars. From this study, the temperature of 40°C and using acetone as a co-solvent was chosen for the coating experiments since all three polymers showed an improved solubility at these conditions.

These results can most probably be explained by the different structures of the polymers. PCL is a semicrystalline polymer that does not have any side groups that can increase the free volume of the polymer and facilitate the penetration of CO_2 molecules into the polymer to dissolve it. Although semicrystalline polymers show lower solubility in SC-CO_2 compared to amorphous polymers, PCL could give the coated surfaces interesting properties due to the crystallinity content and is therefore included in the study. The co-polymers are amorphous and have side chains in the polymer backbone that causes flexibility and increases the free volume. These functional side groups are likely to interact with the CO_2, which results in a higher solubility of this polymer in SC-CO_2.

Spraying of polymers with the RESS technique

The same setup as for the dynamic solubility study was used for the coating experiments and a flow of nitrogen was added next to the restrictor to remove the acetone in the spray jet. Scanning electron microscopy (SEM) was used to study the surface morphology and contact angle measurements (CAM) were performed to determine the advancing contact angle between a water droplet and the surfaces. The advancing contact angle was measured in the centre of the spray pattern on the surfaces and the contact angles are mean values of three measurements on three different surfaces.

Due to the low solubility only small amounts of PCL end up on the surfaces during spraying and the contact angles were around 90°, see figure 1. During the contact angle measurements the water droplet comes in contact with the silica surfaces due to the poor surface coverage. Not all of the particles produced in RESS end up on the silica surfaces when spraying both of the co- polymers. Despite this, the amount of co- polymer on the coated surfaces is greater than for the PCL treated surfaces. Polymer A show advancing contact angles around 130° and from the SEM images it is possible to see a mixture of particles, agglomerates and fibres on the surfaces. The coated surfaces of polymer B had the highest contact angle, around 160° and these surfaces also contains a mixture of particles, agglomerates and fibres.

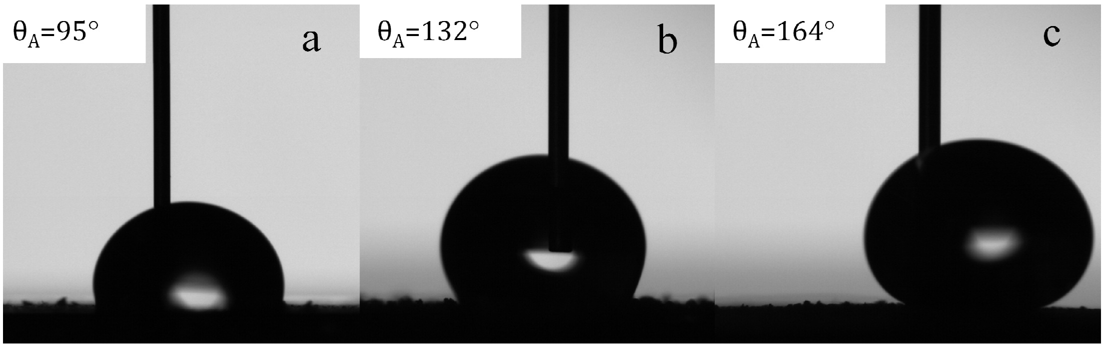

Figure 1: The advancing contact angles of: a. PCL, b. polymer A, c. polymer B.

One way to determine the hysteresis of a surface is to measure both the advancing and receding contact angles, and the difference between those angles is simply the hysteresis. For these surfaces it was not possible to determine the receding contact angle since the water droplet got pinned to the surfaces, which indicate that the surfaces are not superhydrophobic although some surfaces had high advancing contact angles (above 150°).

CONCLUSIONS

In this work, the RESS technique has been used to prepare particles by spraying polymers onto silica surfaces. First, the solubility of PCL and a co-polymer was initially studied with a dynamic solubility method. The solubility of the polymers were improved at 40°C and by using acetone as a co-solvent, therefore these conditions were chosen for the coating experiments. PCL was not soluble enough in SC-CO_2 mixed with acetone in order to obtain uniform coatings. The contact angles of these surfaces were around 90°. Surfaces with higher contact angles, 130° and 160° respectively, were obtained when spraying the co-polymers. These promising surfaces consisted of a variety of particles, fibres and agglomerates.

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