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Supercritical carbon dioxide-soluble polyhedral oligomeric silsesquioxane (POSS) nanocages and polymer surface modification

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ABSTRACT

In this work, a functionalized polyhedral oligomeric silsesquioxane (POSS) has been investigated for its solubility in supercritical carbon dioxide for the first time in literature. POSS nanocages, which can be functionalized with a wide variety of organic substituents, are most commonly studied as nanofillers in polymer nanocomposites and coatings. Solubility of trifluoropropyl POSS in supercritical carbon dioxide has been determined by cloud-point measurements performed in a high-pressure view cell. At temperature and pressure ranges of 308–323 K and 8.3–14.8 MPa, these fluorinated organic–inorganic hybrid nanocage structures exhibit solubility up to 4.4% by weight, which is promising for green material processing applications using the environmentally benign solvent. Solubility of CO_2-philic POSS decreases with increasing temperature, while the solubility isotherms at two different temperatures converge. Choosing the processing conditions from the performed solubility studies, trifluoropropyl POSS–supercritical carbon dioxide system has been applied in high-pressure surface modification of a high-molecular weight, rigid poly(methyl methacrylate) (PMMA). Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) analysis of the processed PMMA sheet show that the functionalized nanoparticles were deposited on the PMMA surface, forming a uniform coating of POSS aggregates. This work proves that functionalized POSS with CO_2-philic groups can be solubilized in supercritical CO_2, which might allow them to be applied in a plethora of materials modification processes using supercritical carbon dioxide.

1. Introduction

Functionalized nanoparticles have been used in polymer processing to enhance thermal, mechanical and barrier properties of polymers. Polymeric nanocomposites with functionalized nanoparticles are prepared mostly by melt-phase compounding, solution blending or in situ polymerization. However, these techniques are associated with a number of processing and environmental problems such as limited nanoparticle dispersion, thermal instability of nanoparticles at high temperatures, volatile organic compound (VOC) emissions of solvents, and limited applicability and scalability of processes [1–4]. In order to engineer, design and tailor nanocomposites for high-technology applications, precise morphology control is an essential challenge. While homogeneous and efficient dispersion of nanoparticles is crucial to obtain high-aspect ratio materials such as thin films and fibers, the nanoparticle agglomeration and poor dispersion issues have become major obstacles in commercialization of nanocomposite polymeric fibers and films. To modify polymeric surfaces with nanostructures, chemical and physical vapor deposition and sol–gel processes have been widely used [5,6]. These techniques, however, can often result in associated environmental concerns due to VOC emissions. While controlling the size and morphology of the particles deposited on the polymeric surface is vital, in solution based techniques due to capillary forces and high-surface tensions, local structural and concentration differences can occur, causing nonuniformity of the nanoparticle shell on the polymeric surface.

Non-toxic, non-flammable, inexpensive, and abundant supercritical carbon dioxide ($scCO_2$) has been used in materials processing with nanoparticles. $scCO_2$ can plasticize a wide range of polymers including poly(methyl methacrylate) (PMMA), polystyrene (PS), polycarbonates (PC), and poly(lactic acid) (PLA), by dissolving in the polymer matrix, decreasing their T_g and allowing their processability [7–11]. In recent studies, $scCO_2$-assisted conventional techniques such as melt extrusion, solvent dissolution or in situ polymerization was used in preparation of polymer nanocomposites reinforced with surface-modified nanoparticles [12–22]. In some of these studies, significant improvement in mechanical properties such as storage modulus and yield stress of the nanocomposites were obtained, which was attributed to better particle dispersion achieved in the polymer matrix with $scCO_2$ treatment, compared to nanocomposites prepared with

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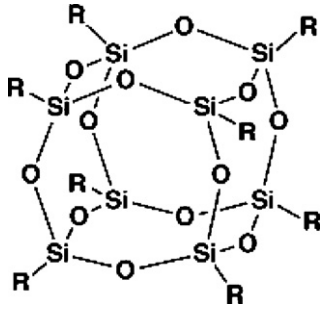

Fig. 1. Polyhedral oligomeric silsesquioxane structure with R functional groups.

conventional techniques [14–16,19]. $scCO_2$ has also been used in order to deposit metal nanoparticles on various substrates including metal oxides, silica, carbon aerogel, or polymers. One common application is to deposit metal nanoparticle precursors with CO_2-philic groups on a substrate, and to form the elemental metal nanoparticle by reduction of the deposited precursor [23]. Metal nanoparticles have also been deposited on surfaces by supercritical CO_2 used as a benign antisolvent, which expands the organic solvent-nanoparticle suspensions, causing the nanoparticles to precipitate on the substrates [24,25].

The objective of our studies on nanoparticles is to determine the $scCO_2$-soluble nanoparticles, and use them in environmentally benign modification of materials with $scCO_2$. Polyhedral oligomeric silsesquioxanes (POSS) are among common nanofillers used to enhance thermal and mechanical properties, flame retardancy, and oxidation resistance of engineering plastics [26–32]. With $(RSiO_{1.5})_n$ formula, where n is generally 8, they have cage structures made of silicon and oxygen (Fig. 1). A wide variety of organic functional groups can be attached to the silicones, which give opportunity to design custom-tailored POSS with the desired chemical and physicochemical properties. In this study, these functional groups are chosen as CO_2-philic moieties, which can allow POSS to solubilize in $scCO_2$. In case they are soluble in this benign solvent, functionalized nanocage structures can be applied in a plethora of green processing of advanced materials with the supercritical fluid.

The solubility of a component in $scCO_2$ is attributed to the component's ability to participate in electrostatic or Lewis-acid base interactions with CO_2 [33–37]. Although being a low-dielectric fluid, CO_2 can exhibit Lewis acid–base interactions due to its quadrupole moment, which also allows CO_2 to exhibit dipole–quadropole or quadropole–quadropole interactions with certain types of functional groups. Fluorinated hydrocarbons are one of the most common CO_2-philic groups incorporated to compounds to increase their solubility in $scCO_2$ significantly. Through high-pressure NMR and theoretical studies, high solubility of most fluorinated compounds was attributed to interactions between the quadrupole moment of CO_2 and the dipoles of fluoroalkanes [38]. On the other hand, more recent ab initio calculations and high-pressure NMR studies suggest that the fluorine atoms act as weak Lewis base sites, while CO_2 acts as a weak Lewis acid in CO_2-fluorocarbon interactions [39,40]. As the entropic contribution, incorporation of highly electronegative fluoroalkane side chains with weak van der Waals forces can increase the free volume of the compound, decrease its cohesive energy density and surface tension, enhancing its solubility in $scCO_2$ [41,42]. In this work, the solubility of trifluoropropyl POSS with CO_2-philic fluoroalkanes, in $scCO_2$ has been studied for the first time, and polymer surface modification with the $scCO_2$-soluble nanomaterials and carbon dioxide has been demonstrated.

2. Experimental

2.1. Materials

Trifluoropropyl POSS, a white-powder solid (Hybridplastics) with a molecular formula of $(C_3H_4F_3)_n(SiO_{1.5})_n$ with $n=8$ was used in the solubility experiments without further purification. Carbon dioxide (99.998%) was obtained from Messer Aligaz. Trifluoropropyl POSS was characterized with DSC (Seteram, DSC 131) and Atomic Absorption Spectrophotometer (Shimadzu, AA6300), to detect its melting point, which was found to be 462 ± 3 K, and residual calcium content, which was found to be 600 ± 14 ppm. Highly cross-linked, very rigid, and high impact resistance PMMA sheets were obtained from Goodfellow, and had a number average molecular weight of 600,000 g/mol, with polydispersity of 4.5. Its ambient-pressure glass transition temperature was measured with DSC as 406 K. The morphology and micro-structural features of the PMMA samples were characterized by field emission scanning electron microscope (FE-SEM, FEI Quanta FEG 450) operated at 20 kV, while Si and F dispersion of trifluoropropyl POSS domains were detected by energy dispersive solid state spectroscopy (EDS), semi-quantitative elemental mapping. Polymer surfaces were sputter-coated with gold, and directly imaged in the electron microscope.

2.2. Experimental set-up

Both the solubility measurements of trifluoropropyl POSS in $scCO_2$ and polymer surface deposition experiments were performed in a high-pressure, jacketed vessel, with two sapphire windows (Fig. 2). The temperature of the high-pressure vessel was controlled with a water circulating heater (Cole-Parmer Polystat Circulating Bath). A Teledyne ISCO pump (model 260D), was used to charge a measured amount of liquid CO_2 into the vessel. The temperature of the pump was also controlled with a water circulating heater (Cole-Parmer Polystat Circulating Bath) to keep the charged CO_2 at constant temperature. The temperature of the ISCO pump reservoir was controlled within ± 0.2 K, and its pressure was measured to within ± 0.05 MPa. A thermocouple along with a meter (Omega Engineering, GTMQSS-062G-6 and DP462) and a pressure transducer along with a strain meter (Omega Engineering, PX4100-6KGV and DP25B-D-230) were used to measure the temperature and pressure of the contents of the vessel. Temperature and

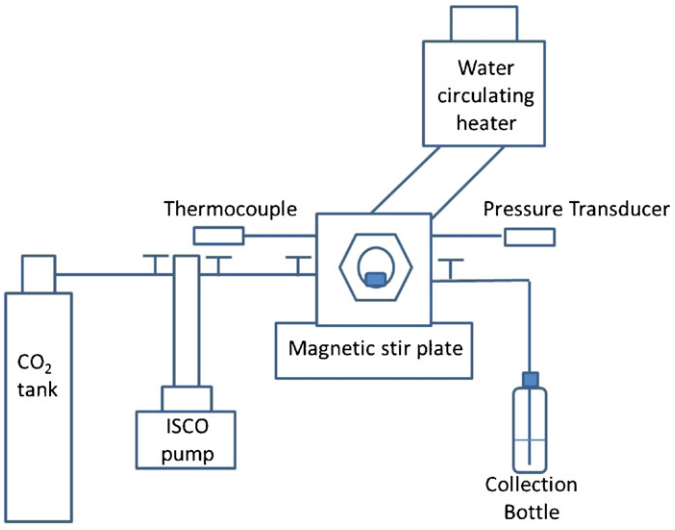

Fig. 2. Experimental set-up for cloud and bubble point measurements and surface deposition experiments.