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Effects of functional groups on the solubilities of polyhedral oligomeric silsesquioxanes (POSS) in supercritical carbon dioxide

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The phase behavior of the binary systems containing CO_2 and various hybrid polyhedral oligomeric silsesquioxanes (POSS) with different functional groups were investigated. A high-pressure view cell was used to measure the dew-points or cloud-points at temperatures between 308 and 323 K, up to 30 MPa. Among the studied POSS structures, methacryl, isooctyl and octaisobutyl POSS were observed to form homogenous solutions with CO_2, while octamethyl POSS was found to be insoluble in the supercritical fluid. The solubilities of both methacryl and isooctyl POSS in $scCO_2$ decrease with increasing temperature, while isooctyl POSS exhibits nearly an order of magnitude higher solubility than methacryl POSS at both temperatures. The octaisobutyl POSS-CO_2 binary system exhibits a crossover pressure, below which the solubility of the component decreases with increasing temperature. Above this pressure, as the temperature is increased, the solubility of POSS in $scCO_2$ increases. These results show that the functional groups of POSS affect its solubility in $scCO_2$ and the phase behavior of the POSS-CO_2 binary system significantly. The $scCO_2$-soluble POSS can be implemented in environmentally benign material processing applications using the supercritical fluid.

1. Introduction

POSS are commonly used, cage-like structured materials, which are represented by the chemical formula of $(RSiO_{1.5})_n$, with n being generally equal to 8 [1]. The hybrid property of POSS is due to its inorganic (silica) and organic groups (R) attached to each Si atom on the cage structure [2]. They have been widely used in polymer applications as nanofillers [3], and in drug delivery systems and tissue implants [4–7]. The functional organic groups are responsible for interactions of POSS with polymer chains. Thus, these groups enhance the compatibility of POSS molecules with the polymer and allow their homogeneous dispersity in the polymer matrix [1,8]. Many properties of the polymeric materials such as flame retardancy, oxidation resistance, thermal stability, conductivity, luminance and current efficiency can be improved by addition of POSS into the polymer matrix [9–13].

Being abundant, inexpensive, non-toxic and non-flammable, supercritical carbon dioxide ($scCO_2$) has been increasingly used in material processing applications [14–19]. One of the most important advantages is that it can decrease or eliminate the use of organic solvents in chemical processes. Thus, it can prevent the emissions of volatile organic compounds which are associated with organic solvent use. $ScCO_2$ is commonly used in surface coating and polymer processing applications such as polymer foaming, polymer impregnation, and crystallization of plastics [20–26]. Additionally, with its low critical temperature, $scCO_2$ processes require low operating temperature and therefore, can prevent degradation of the temperature-sensitive materials.

In order to develop $scCO_2$ processing techniques applying novel materials such as POSS, thermodynamic phase behaviors of these materials with CO_2 are needed to be studied. Recently, POSS with CO_2-philic fluoroalkyl groups (F-POSS) was investigated for its solubility in $scCO_2$ [27]. Solid–vapor phase equilibrium curves of the binary system were determined with the cloud point measurements. At temperature and pressure ranges of 308–323 K and 8.3–14.8 MPa, F-POSS exhibits solubility in $scCO_2$ up to 4.4% by weight and 0.17% by mole. Its solubility in $scCO_2$ decreases with increasing temperature. Using the obtained phase behavior data of F-POSS-CO_2 binary system, process conditions were determined for surface coating application without use of any organic solvents. In a later study, the solubility data were used to design a process where a POSS fiber was extracted to create a microchannel in an aerogel for optofluidic applications [28]. Recently there have been few studies which use POSS with $scCO_2$ in material processing applications; however these studies have not investigated the phase equilibria of the used POSS-CO_2 systems

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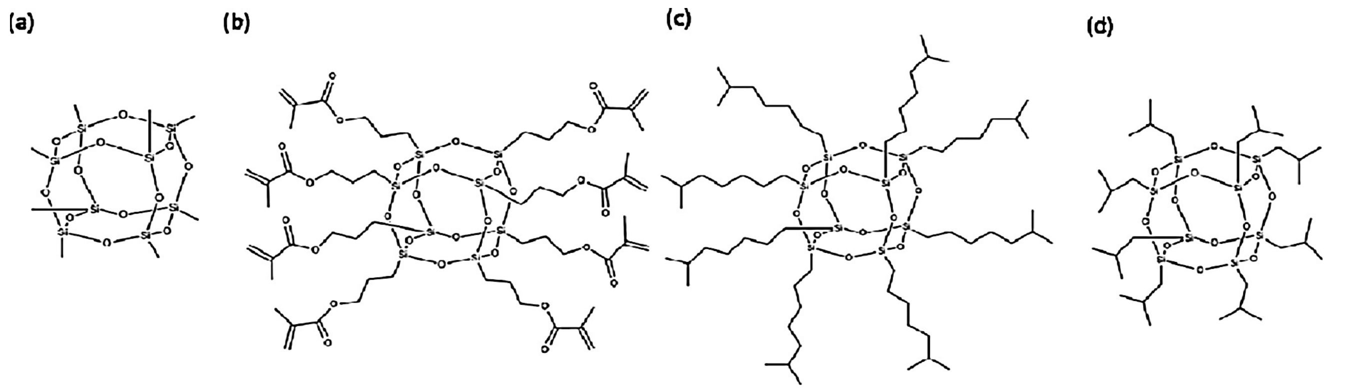

Fig. 1. Chemical structures of (a) octamethyl POSS, (b) methacryl POSS, (c) isooctyl POSS (d) octaisobutyl POSS.

[29–32]. In this work, solubility data of various POSS with different organic functional groups in supercritical carbon dioxide have been presented. The studied POSS are octamethyl, methacryl, isooctyl and octaisobutyl POSS, which are among the commonly used POSS in the material processing applications. They are mostly used as fillers in polymeric blends and nanocomposites [33–35]. Other applications include surface modification and coating [36,37] and formation of polymeric films [38].

2. Experimental

2.1. Materials

Octamethyl POSS (94.0%, Fig. 1a), methacryl POSS (97.2%, Fig. 1b), isooctyl POSS (99.0%, Fig. 1c), and octaisobutyl POSS (99.4%, Fig. 1d) were supplied from Hybridplastics. All the POSS types were used in the experiments without further purification. Carbon dioxide (99.9%) was supplied from Linde. Octamethyl POSS and octaisobutyl POSS with bulk densities of 0.59 g/cm^3 and 0.63 g/cm^3, respectively, are in powder form. Isooctyl POSS and methacryl POSS are viscous liquids with densities of 1.01 g/cm^3 and 1.2 g/cm^3 and viscosities of 19 and 18 Poise at 298 K, respectively, (both the density and viscosity data were supplied by the manufacturer). With DSC (Shimadzu DSC-60) and TGA (Shimadzu DTG-60H) analysis it was observed that both of the solid POSS start to degrade upon heating and exhibit at least 10% weight loss before they melt. 10% weight loss temperatures of octamethyl POSS and octaisobutyl POSS were observed in TGA analysis as 513 K and 538 K, respectively. The solubilities of POSS in supercritical carbon dioxide have been measured by cloud or dew point experiments.

2.2. Experimental set-up

The dew and cloud point measurements of POSS-CO_2 binary systems were performed using a high-pressure set-up, which is represented schematically in Fig. 2. The set-up contained a custom-made jacketed stainless steel high-pressure vessel with two sapphire windows, a rupture disc, and two needle valves. The inner volume of the high-pressure vessel is 46.15 ± 0.07 cm^3. A syringe pump (Teledyne ISCO-260D) was used to charge CO_2 into the vessel. The temperature of the ISCO pump reservoir was controlled with a water circulating heater (Polyscience, 9112) within a range of ±0.01 K. The syringe pump pressure accuracy was within ±0.05 MPa. Prior to the measurements, the syringe pump was loaded with CO_2 from a CO_2 cylinder with dip tube. A thermocouple (Omega Engineering KMQXL-IM150U-150) was used to measure the temperature of the high-pressure vessel contents to an accuracy of ±0.5 K. The temperature of the vessel was controlled by a water circulating heater (Polyscience, 9112) within a range of ±0.01 K. The vessel pressure was measured using a pressure transducer (Omega Engineering PX419) to an accuracy of ±0.03 MPa. The set-up included a magnetic stir plate to mix the contents of the vessel continuously.

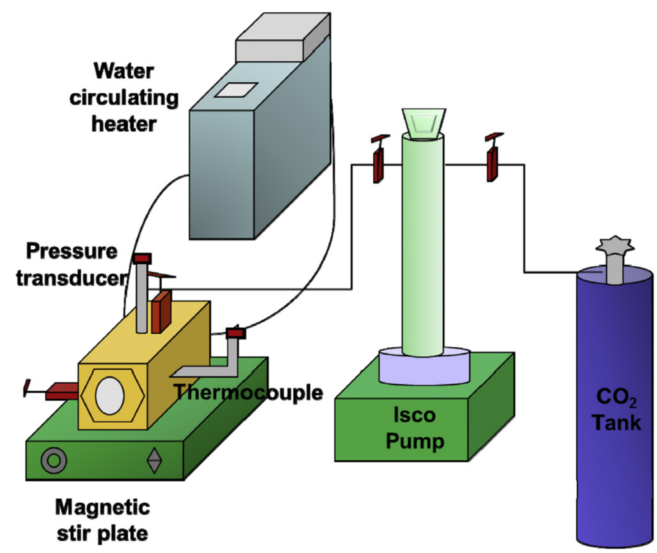

Fig. 2. Experimental set-up for the solubility measurements.

2.3. Experimental procedure

The solubilities of POSS in $scCO_2$ have been obtained by dew and cloud point measurements for liquid POSS and solid POSS, respectively. Both measurement procedures were identical except the phase of the solute that segregated from the homogenous mixture. Initially, the high pressure vessel was loaded with POSS, which was weighed to an accuracy of ±0.0001 g. The vessel was sealed and its temperature was increased to the desired value by the water circulating heater. The temperature of the ISCO pump reservoir was also set to the desired value. Next, the vessel was connected to the syringe pump with a high-pressure tubing carrying a check valve to avoid reverse flow. After setting the pressure of the ISCO pump to the desired value, the tubing between the vessel and the syringe pump was loaded with CO_2 using the syringe pump operating at constant-pressure mode. Before introducing CO_2 into the vessel through the vessel inlet valve, the volume of the pump reservoir filled with CO_2 was recorded. Next, CO_2 was loaded into the vessel slowly until the vessel pressure was equalized to the syringe pump pressure. The inlet valve was then closed, and the volume of the pump reservoir filled with CO_2 was recorded one more time to calculate the volume displacement, which gave the volume of the