Carbon Dioxide-Philic Hybrid Polyhedral Oligomeric Silsesquioxanes

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ABSTRACT

In this work, we have investigated the solubility of various hybrid polyhedral oligomeric silsesquioxanes (POSS) in supercritical carbon dioxide ($scCO_2$) at 308 and 323 K, up to 300 bar. POSS are used in polymer processing in order to improve the properties of the material such as flame retardancy, oxidation resistance, conductivity, luminance and current efficiency. They are also used in drug delivery systems and tissue implants to enhance the mechanical strength, bioactivity and thermal stability of biomaterials. In case CO_2-philic groups are attached to POSS, the hybrid structures can exhibit solubility in $scCO_2$. The types of POSS studied include methyl, isooctyl, and methacryl POSS. Except the one with methyl groups, the studied POSS exhibit solubility in supercritical carbon dioxide, which decrease with increasing temperature. The phase equilibria curves of the binary systems have been obtained, and the solubility data is currently used in the design of environmentally friendly material processing applications using $scCO_2$.

Key Words: Supercritical carbon dioxide, Solubility, Polyhedral Oligomeric Silsesquioxane

INTRODUCTION

POSS are cage-like structured materials, which have $(RSiO_{1.5})_n$ chemical formula and hybrid property due to their inorganic (silica) and organic (carbon) molecules [1]. Functional groups attached to Si atoms are represented by R, and n is generally 8. POSS have been widely used in polymer applications and recently in drug delivery systems and tissue implants [1-6]. In polymer applications, POSS nanocages must carry organic functional groups attached to Si atoms, which allow their interactions with the polymer chains. This improves their compatibility with the polymer, and serves to increase their dispersion within the polymer matrix. When added to polymers, POSS can enhance many properties of the material, such as the mechanical properties, thermal stability, flame retardancy, oxidation resistance, conductivity and current efficiency.

Supercritical carbon dioxide ($scCO_2$), which is non-toxic, non-flammable, inexpensive, and abundant has been applied in polymer processes as a plasticizer, allowing the processibility of the polymers by decreasing their glass transition temperature. Research on solubility of novel materials in supercritical carbon dioxide ($scCO_2$) contributes to development of environmentally friendly material processing applications using $scCO_2$ as a green solvent. In case POSS is soluble in $scCO_2$, it can be used in various polymer applications using the green solvent, which can prevent emissions of volatile organic compounds (VOC) encountered in conventional methods using organic solvents. We have been investigating the solubility of POSS with various groups in $scCO_2$, and the first type we studied was trifluoropropyl POSS for which the solid-vapor phase equilibrium curves were obtained with the cloud point measurements [1]. Following the phase equilibrium studies, trifluoropropyl POSS-CO_2 single phase solution was applied for surface coating of a high molecular weight, rigid polymethyl methacrylate. Without the use of any organic solvents, a homogeneous POSS film was obtained on the surface of the polymer. Our studies have continued with solubility studies of various POSS containing different functional groups such as methyl, methacryl, isooctyl.

MATERIALS AND METHODS

The solubility measurements of POSS in $scCO_2$ are performed in a high-pressure, jacketed vessel, with two sapphire windows (Fig. 1). A Teledyne ISCO pump (model 260D) is used to load certain amount of liquid CO_2 into the vessel. Water circulating heater (Polyscience) is connected to the system to control the temperature of the high-pressure vessel. The temperature of the ISCO pump reservoir is also controlled with the water circulating heater to charge CO_2 at constant temperature. A thermocouple along with a meter (Omega Engineering) is used to measure the temperature, and a pressure transducer along with a strain meter (Omega Engineering) is used to measure the pressure of the vessel.

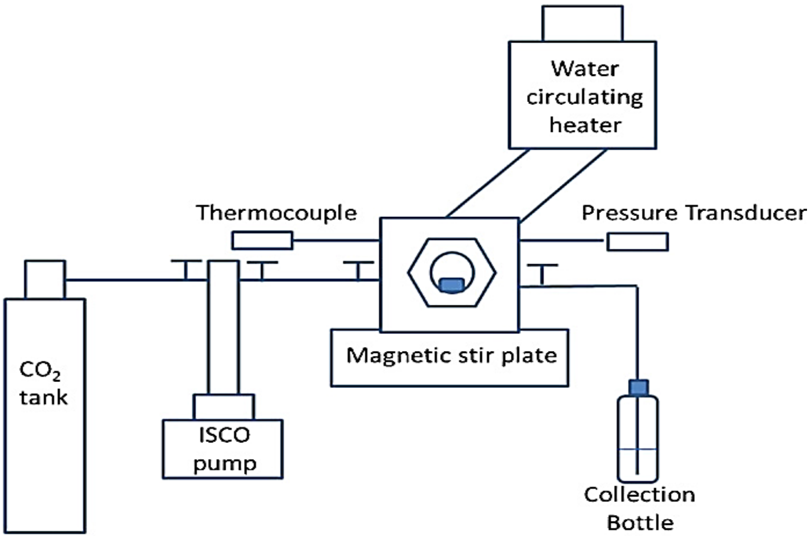

Figure 1. Experimental set-up for dew point measurements [1].

In solubility studies, octamethyl POSS, isooctyl POSS, and methacryl POSS, (Hybridplastics) and carbon dioxide (Linde) (99.99%) have been used. Isooctyl POSS and methacryl POSS are viscous liquids, while octamethyl POSS is a powder. POSS solubilities in $scCO_2$ have been obtained by dew or cloud point measurements. Once the system is loaded with POSS and carbon dioxide, all loaded POSS is provided to dissolve in the supercritical carbon dioxide by continuous stirring with a magnetic stirrer. When the system forms a single phase, depressurization of the system is started at a very low speed, during which the temperature of the system is maintained constant. A dew point or a cloud point is observed once the liquid or solid POSS separates from the solution, and the system is visibly clouded at the phase separation. The pressure, at which the separation occurs, represents the highest possible pressure in the liquid-vapor or solid-vapor phase equilibria of the loaded total concentration of POSS-carbon dioxide system at constant temperature.

RESULTS

Octamethyl POSS is insoluble in $scCO_2$, while solubility of methacryl POSS and isooctyl POSS in $scCO_2$ are represented in Figure 2 and Figure 3 respectively. Both figures show the liquid-vapor (L-V) phase equilibrium curves of POSS-CO_2 binary systems at 308 and 323K. In Figure 2, the highest solubility of methacryl POSS measured is about $4x10^{-4}$ mol fraction at 308 K and 285 bar. The region on the left side of the L-V equilibrium curve of the binary system, e.i. lower concentration and higher pressure region, represents the conditions at which the binary mixture exists in a single phase, where POSS is completely dissolved in $scCO_2$. As the temperature of the binary system increases, the pressure and so the density of supercritical CO_2 has to be increased to solubilize the POSS completely. The required system pressure to bring the binary system with $1x10^{-4}$ mole fraction of POSS to a single phase is about 200 bar at 308 K, while it increases to 260 bar at 323K.

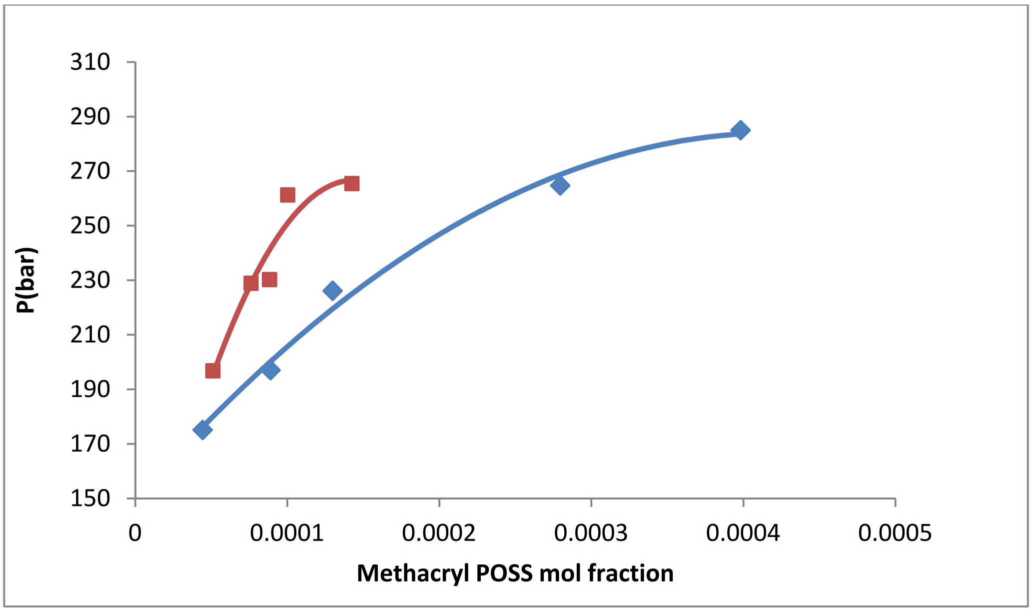

Figure 2. The dew point pressures of Methacryl POSS–CO_2 binary system at 308 K (◆) and 323K (■)

In literature, the interaction between the carbonyl compounds connected to hydrocarbons and carbon dioxide is explained with the results of Ab Initio calculations and IR spectroscopic analysis [7, 8]. The solubility of carbonyl containing materials in $scCO_2$ is attributed to the Lewis acid-base interactions between the electron donor carbonyl and the electron acceptor carbon dioxide. It is also indicated that the weak hydrogen bond between the hydrogen atom attached to the carbonyl carbon in the carbonyl compounds and oxygen atoms in carbon dioxide is cooperative interactions for solubility in $scCO_2$. The solubility of methacryl POSS in $scCO_2$ can be due to these specific interactions between the carbonyl groups and CO_2.

The L-V phase equilibrium curves of isooctyl POSS-CO_2 binary system are given in Figure 3. The highest solubility of isooctyl POSS in CO_2 measured is about $6x10^{-4}$ mole fraction at 170 bar. Figure 2 and 3 show that the solubility of isooctyl POSS is higher compared to that of methacryl POSS; at 308K, to dissolve $4x10^{-4}$ mole fraction of methacryl POSS the system pressure has to be 285 bar, while it is about 150 bar for isooctyl POSS. As the temperature increases, the solubility of isooctyl POSS in $scCO_2$ decreases. Similar to the methacryl POSS-CO_2 binary system, the system pressure, so that the density of CO_2 has to be increased to maintain the system in a single phase with increasing temperature. At 308 K to dissolve isooctyl POSS at $6x10^{-4}$mole fraction, the system pressure has to be about 165 bar, while at 323K, for complete solubility of POSS, the required pressure is about 200 bar.

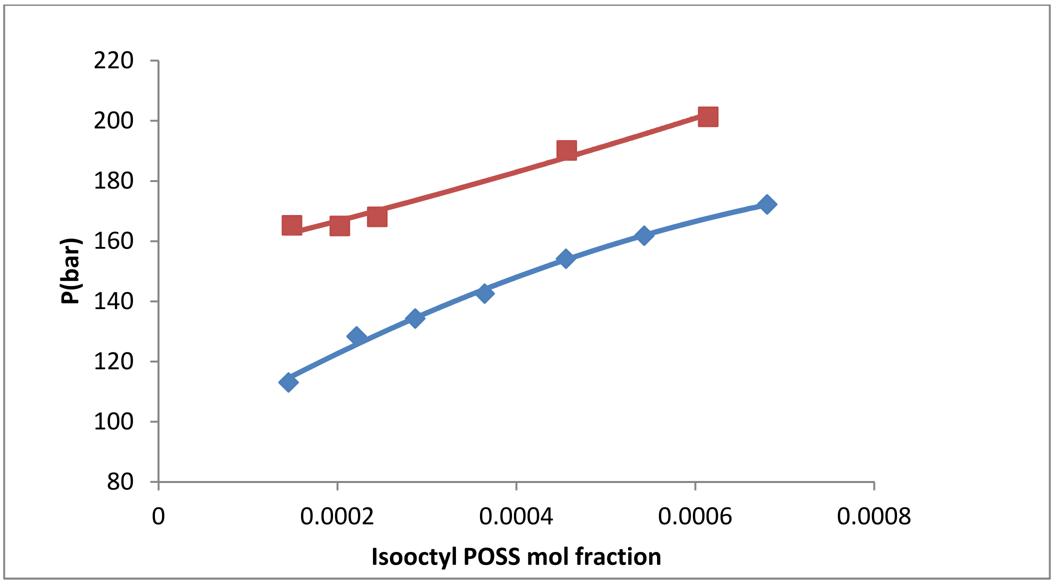

Figure 3. The dew point pressures of Isooctyl POSS–CO_2 binary system at 308 K (◆) and 323 K (■)

When the methyl groups which are attached to silicon atoms in POSS are replaced with the branched isooctyl groups, the component becomes soluble in supercritical carbon dioxide. When branched alkyl side groups are attached to CO_2-philic polymers, their solubility in $scCO_2$ increases due to the increase in entropy of mixing [9]. Similarly, solubility of isooctyl POSS in $scCO_2$ can be attributed to the branched structure of the attached groups of POSS.

CONCLUSION

POSS with methyl, methacryl, and isooctyl groups attached to the silicon atoms have been investigated for their solubility in supercritical carbon dioxide. The dew points of the POSS-CO_2 binary systems have been measured at 308 and 323 K, and the corresponding liquid-vapor phase equilibrium curves have been obtained. Both isooctyl and methacryl POSS are soluble in $scCO_2$, with isooctyl POSS exhibiting nearly an order of magnitude higher solubility than methacryl POSS. Octamethyl POSS has no solubility in $scCO_2$, which shows that solubility of POSS in $scCO_2$ is either due to the specific interactions between the groups attached to the silicon atoms and CO_2 as in the case of methacryl POSS, or the entropic contributions as in the case of isooctyl POSS with branched alkyl groups. The solubility of both methacryl and isooctyl POSS in supercritical carbon dioxide decrease with increasing temperature. Therefore, the system pressure, thus the density of CO_2 has to be increased to bring the system to single phase with all the POSS solubilized in $scCO_2$.

REFERENCES

[1] Dilek, C., J. Supercritical Fluids, 73, **2013**, p.171
[2] Leu, C.-M., Reddy, G.M., Wei, K.-H., Shu, C.-F., Chem. Mater,. 15 (11), **2003**, p.2261
[3] Chew, S. L. , Wang, K. , Chai, S. P. Goh, K. L., J Mater Sci: Mater Med, 22, **2011**, p.1365
[4] Kannan. R.Y., Salacinski, H.J., Odlyha, M., Butler, P.E., Seifalian, A.M., Biomaterials, 27 (9), **2006**, p.1971
[5] Zhang, W., Li, X., Guo, X., Yang, R., Polymer Degradation and Stability, 95 (12), **2010**, p.2541
[6] Wei, W., Xiao, S., & Shih, I., Applied Surface Science, 221, **2004**, p.358
[7] Kazarian, S.G., Vincent, M.F., Bright, F.V., Liotta, C.L., Eckert, C.A., J. Am. Chem. Soc., 118, **1996**, p.1729
[8] Raveendran, P., Wallen, S., J. Am. Chem. Soc., 124, **2002**, p.12590
[9] Fink, R., Hancu, D., Valentine, R., Beckman, E.J., J. Phy. Chem. B, 103, **1999**, p.6441