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APPLICATION OF POLYMER SWELLING BY scCO_2 TO THE SYNTHESIS OF POLYMER/METAL NANOCOMPOSITES

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Abstract. Polymer swelling by scCO_2 was mainly studied to understand many industrial processes, especially in the field of pharmacy for drug delivery (impregnation) and also polymer processing by CO_2 -assisted extrusion. We have studied here another application of polymer swelling by scCO_2 for the synthesis of nanocomposites. The selected model system was the direct synthesis of copper nanoparticles in a poly(ethylene glycol) matrix (PEG). The study of the formation of nanostructures in polymer matrix is constituted of three main steps: i) thermodynamical behaviour of the polymer/ CO_2 system, ii) viscosity of the polymer/ CO_2 system and iii) nucleation and growth of copper nanoparticles.

First, the thermodynamical behaviour of the PEG/ CO_2 system was studied by *in situ* IR spectroscopy. This method gives accurate values of the polymer swelling by scCO_2 but also of the CO_2 sorption in the polymer. For example, at 40°C -15MPa, the swelling of PEG is equal to 35% for a CO_2 solubility of 23 wt%. Secondly, we have developed an original falling ball viscometer for the determination of PEG viscosity as a function of CO_2 density. A good knowledge of the polymer/ CO_2 system is finally used for the control of formation of copper nanoparticles. This formation was followed by *in situ* UV - visible spectroscopy and characterized by transmission electron microscopy.

Introduction

Polymer swelling by scCO_2 was mainly studied to understand many industrial processes (in pharmacy for drug delivery [1] or in polymer processing by CO_2 -assisted extrusion [2,3]). Curiously, the approach of polymer swelling by scCO_2 was occasionally used to functionalize polymer matrixes with inorganic nanoparticles (NPs) to produce organic-inorganic nanocomposites [4-8]. For example, platinum/poly(4-methyl-1-pentene) (PMP) composites [4] have been obtained by impregnation and reduction of CODPtMe_2 in presence or not of CO_2 and H_2 . Palladium NPs have also been stabilized in dendritic structures [8].

Based on the numerous application fields of these organic-inorganic nanocomposites (automotive, aeronautic, pharmacy, chemistry...), we have developed a complete method using supercritical fluids to understand and control the formation of NPs in polymer matrixes. This method is mainly based on three steps:

- i) thermodynamical behaviour of the polymer / CO_2 system
- ii) viscosity of the polymer / CO_2 system
- iii) nucleation and growth of nanoparticles

The selected system for the development of the method of formation of NPs in polymer matrix is a poly(ethylene glycol) matrix (PEG) nanostructured with copper NPs. In order to correlate nucleation and growth phenomena of copper nanoparticles formation with the thermodynamical behaviour of the PEG/CO₂ system, we have studied successively: i) the swelling of PEG by scCO₂ and the CO₂ sorption in PEG by *in situ* IR spectroscopy, ii) the viscosity of PEG/CO₂ mixture with an original falling ball viscometer and iii) the formation of copper NPs in the PEG matrix.

Study of PEG Swelling by scCO₂ with *in situ* IR Measurements

Principle of the Experiments. Poly(ethylene glycol) is a semi crystalline polymer with a glass transition temperature of -70°C and a melting temperature of 6°C. PEG (Aldrich, France) with average molar mass of 400g/mol was used in this study.

The near infrared absorption experiments were performed using a home made stainless steel cell equipped with four cylindrical sapphire windows with a pathlength of 7 mm [9]. The heating of the cell was performed using cartridge heaters disposed in the periphery of the body of the cell. Thanks to a hydraulic pressurizing system, the pressure can be raised up to 50 MPa with an absolute uncertainty of ± 0.1 MPa and a relative error of $\pm 0.3\%$.

The cell was filled with PEG and heated up to the desired temperature (Fig. 1a). Before heating, the cell was pumped under vacuum in order to remove any trace of water in the polymer. The spectra were recorded for the neat polymer. CO₂ was then added up to the highest desired pressure (Fig. 1b). The system was kept under isobaric and isothermal conditions for a long period of time (from few hours at high temperatures up to 2 or 3 days at 40°C) to reach the thermodynamical equilibrium (Fig. 1c). After recording the spectrum, the pressure was decreased to a lower value. For each pressure, the equilibrium was considered to be reached when no change of the spectral bands was noticed.

Fig. 1: Study of PEG swelling by scCO₂ with *in situ* IR spectroscopy: a) IR measurement of PEG, b) injection of CO₂ in the desired conditions, c) *in situ* measurement of PEG swelling by scCO₂

Results. IR spectra of PEG [10,11] subjected to CO₂ were recorded for a pressure of 15MPa and 3 temperatures: 40, 100 and 150°C.

The PEG swelling was determined from the variation of the maximum absorbance of a PEG peak centered at 4855 cm⁻¹. Using the intensities of a band of CO₂ sorbed in PEG (combination mode of the CO₂, $\nu_1+2\nu_2+\nu_3$ at 4960 cm⁻¹), it is possible to determine the mass percentage of CO₂ incorporated into the polymer using the following equations.

The concentrations of polymer before (C_0) and after exposure to CO₂ (C) are given by the Beer-Lambert law (Eq. 1 and Eq. 2) [6].

$$A_0 = \epsilon C_0 l. \quad (1)$$

$$A = \epsilon C l. \quad (2)$$

If V is the volume of the polymer before exposure to gas and $V + \Delta V$ the volume of the polymer during exposure to gas, it is possible to write (Eq. 3):

$$\frac{C_0}{C} = \frac{V + \Delta V}{V} = 1 + \frac{\Delta V}{V} = 1 + S \quad (3)$$

The swelling of the polymer is obtained by combining these equations (Eq. 4).

$$S = \frac{A_0}{A} - 1 \quad (4)$$

The concentration of CO₂ incorporated into PEG (C_{CO₂}) is given by the Beer-Lambert law using the integrated absorbance of the $\nu_1+2\nu_2+\nu_3$ CO₂ band at 4960cm⁻¹. For a comparison with literature data, CO₂ mass sorption incorporated into polymer matrix is given by Eq. 5 where ρ_{pol} is the polymer density.

$$\%massCO_2 = \frac{C_{CO_2}}{C_{CO_2} + \frac{\rho_{pol}}{1+S}} \quad (5)$$

Fig. 2 shows the variations of PEG swelling and CO₂ mass sorption in PEG at 15MPa for 3 temperatures (40°C, 100°C and 150°C).

Fig. 2: Swelling of PEG (♦) and CO₂ weight percentage (■) as a function of temperature at 15MPa

At constant pressure, an increase of temperature causes a decrease of both the weight percentage of CO₂ incorporated into PEG and its swelling. This could be explained by a weakening of the CO₂-PEG interactions. The maximum swelling (35%) and weight percentage of CO₂ (about 22 wt%) are obtained at 40°C-15MPa [10].

In addition to the study of the swelling of PEG by scCO₂, viscosity has also been investigated. Indeed, it is an important parameter for the understanding of the nucleation and growth phenomena of NPs [12].

Viscosity of the PEG/CO₂ System

Description of the Viscometer. The viscosity of PEG/CO₂ mixtures has been measured as a function of temperature (100°C and 150°C) and pressure (up to 20MPa) with an original falling ball viscometer. It is important to underline that it is not easy to perform viscosity measurements under pressure and temperature. The principle of the viscometer consists in observing the fall of a bead in an open tube immersed in a homogeneous medium (here PEG + CO₂) and in measuring the time of its fall (Fig. 3).

Sapphire windows allow the lighting of the inside of the enclosure and the detection of the fall of the bead in the tube by a digital camera. The tube diameter depends on the diameter of the bead and

allows a restricted flow fall of the bead in the fluid. Here, the tube has a diameter equal to 2.17 mm for a diameter of alumina bead of 2 mm.

In a typical experiment, the glass vessel is filled with the polymer. The enclosure is heated at the desired temperature and CO₂ is added up to the desired pressure. Agitation allows equilibrium to be reached faster. The bead distributor is operated and the fall of the bead is recorded thanks to the camera.

Fig. 3: Scheme of the falling ball viscometer

By using the classical correlation for the friction factor ($f = 16/Re$) for flow in tubes, the viscosity can be estimated in measuring the terminal falling velocity of the bead. This value has to be corrected by the way of a simulation (COMSOL®) or a correlation which takes into account the specific form of the velocity distribution near the bead.

Results. Results are presented in fig. 4.

Fig. 4: Evolution of PEG viscosity saturated by CO₂ at 100°C (■) and 150°C (◆).

As expected, incorporation of CO₂ into PEG decreases its viscosity. Indeed, when pressure increases, CO₂ wt.% incorporated in polymer matrix increases and the volume of the mixture increases. This leads to a decrease of the viscosity of the 'PEG/CO₂' mixture.

Formation of Copper NPs into the PEG Matrix

Experimental Procedure. A copper precursor (copper (II) acetylacetonate, Cu(acac)₂) is first mixed with the PEG. The reactor is charged with the solution. Then, the system is heated and a CO₂ (with or without H₂) pressure is applied to obtain decomposition of the precursor in supercritical conditions.

In situ measurements by UV-visible spectroscopy were also performed to study the kinetics of formation of the copper NPs. The same cell as for IR measurements was used with an UV-Visible source. We follow the apparition and the evolution of copper plasmon band between 500 nm and 600 nm.

Results. Three series of experiments were performed: (a) decomposition in scCO₂, (b) decomposition without CO₂ and (c) decomposition in scCO₂/H₂ mixture. The duration of each experiment was 2h. High Resolution Transmission Microscopy was performed to characterize the composition, the size and size distribution of nanoparticles in the PEG matrix (figure 4).

Figure 4: Micrographs TEM of ‘copper nanoparticles / PEG’ nanocomposites obtained in CO₂, CO₂ / H₂ and without CO₂ media

While copper nanoparticles (4 nm diameter), distributed in the polymer matrix, are obtained in scCO₂, larger particles (200 nm diameter) are formed without CO₂. This difference is attributed to the homogenization of the polymer/precursor solution in scCO₂. In presence of H₂, the size of the copper particles is observed to be around 50 nm which confirmed the faster decomposition of copper precursor in CO₂/H₂ medium comparing with scCO₂. High Resolution Transmission Electron Microscopy shows the interest of decomposition in scCO₂.

The evolution of the plasmon band of copper nanoparticles was followed by *in situ* UV-Visible spectroscopy. This method allows a determination of the decomposition temperature of the precursor through the formation of copper nanoparticles. Copper (II) acetylacetonate is decomposed at 200°C in scCO₂ [13]. It appears from the UV-Visible study that, in PEG matrix saturated by scCO₂, copper formation occurs at 110°C with or without CO₂.

Conclusions

We have reported here a complete method for the optimisation of the synthesis of inorganic NPs in polymer matrixes, especially in this study, copper NPs in a PEG matrix. Thermodynamical behaviour of the PEG/CO₂ system has been studied by *in situ* IR spectroscopy. We have obtained accurate values of CO₂ mass percentage sorbed in PEG. For example, at 40°C-15MPa, the swelling of PEG is equal to 35% for a CO₂ solubility of 22 wt%.

By knowing the polymer swelling by scCO₂, it is possible to determine the viscosity of PEG/CO₂ solutions by an original falling ball viscosimeter. We have confirmed the reduction of PEG viscosity under scCO₂ conditions. This study allows us to better understand the nucleation and growth phenomena of copper nanoparticles in polymer matrix.

Finally, kinetics of copper nanoparticles formation in the polymer matrix was quantified by UV - visible spectroscopy with the observation of the copper resonance plasmon band. The copper precursor was observed to be totally decomposed in a PEG matrix at 110°C after 1h whereas a temperature equal to 200°C was necessary to obtain copper in scCO₂. For example, copper nanoparticles, 4 nm in diameter and distributed in the polymer matrix, were obtained in a scCO₂ medium.

All these parameters give an accurate knowledge of the nanocomposite system in order to optimize the synthesis (size and dispersion) of copper nanoparticles directly in the polymer matrix.

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