AN INNOVATIVE APPLICATION OF POLYMER SWELLING BY scCO$_2$: THEIR NANOSTRUCTURATION WITH INORGANIC NANOPARTICLES

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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 or polymer processing by CO$_2$-assisted extrusion. Curiously, the approach of polymer swelling by scCO$_2$ was just occasionally used to functionalize polymer matrixes with inorganic nanoparticles to produce organic-inorganic nanocomposites, materials with applications in automotive, aeronautic, pharmacy … As a model system, we have here studied a nanocomposite constituted of copper nanoparticles synthesized directly in a Hydroxytelechelic PolyButadiene (or HTPB) polymer matrix. A procedure of polymer nanostructuration was developed and is based on three steps. First, the thermodynamical behaviour of the system HTPB / CO$_2$ system is studied by IR spectroscopy. This method gives accurate values of the polymer swelling by scCO$_2$. At 40°C - 15MPa, the swelling of HTPB is equal to 16% what is lower than for PolyEthyleneGlycol (35% at 40°C - 12MPa). Secondly, an original falling ball viscosimeter is developed to determine the evolution of HTPB viscosity depending on CO$_2$ density. A good knowledge of these parameters is necessary to control the formation of copper nanoparticles (size and dispersion in the polymer matrix) that can be followed by *in situ* UV - visible spectroscopy.

INTRODUCTION

Polymer swelling by scCO$_2$ was mainly studied to understand many industrial processes, especially in the field of pharmacy for drug delivery[1] or polymer processing by CO$_2$-assisted extrusion[2,3]. Curiously, the approach of polymer swelling by scCO$_2$ was just occasionally used to functionalize polymer matrixes with inorganic nanoparticles to produce organic-inorganic nanocomposites[4,5,6,7]. 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$_2$.
Indeed, the interaction of polymer with scCO$_2$ provides unique opportunities for the preparation of nanostructured materials. Based on the numerous application fields of these organic-inorganic nanocomposites (automotive, aeronautic, pharmacy, chemistry…), we have developed a complete method using supercritical fluids for the synthesis of polymer / metal nanocomposites, based on three steps:

- Thermodynamical behaviour of the polymer / CO$_2$ system
- Viscosity of the polymer / CO$_2$ system (linked to nucleation and growth phenomena of nanoparticles formation)
- Nucleation and growth of nanoparticles

For this study, the selected nanocomposite is constituted of a polymer matrix of HydroxyTelechelic PolyButadiene nanostructured with copper nanoparticles. In order to correlate nucleation and growth phenomena of copper nanoparticles formation with the thermodynamical behaviour of the HTPB/CO_2 system, we have studied the swelling of HTPB by $scCO_2$ based on IR spectroscopy and quantized the viscosity of HTPB/CO_2 mixture with an original falling ball viscosimeter.

INFRARED MEASUREMENTS OF HTPB SWELLING BY $scCO_2$

Principle of experiments. Hydroxytelechelic PolyButadiene (figure 1), oligomer, has a glass transition temperature equal to -90°C and average molar mass of 2600 g/mol.
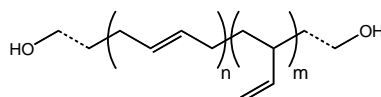
Figure 1. HTPB

The near infrared absorption experiments were performed using a home made stainless steel cell equipped with four cylindrical sapphire windows with a pathlength of 6.7 mm. The heating of the cell was performed using cartridge heaters disposed in the periphery of the body of the cell. The cell was connected via a stainless steel capillary to a hydraulic pressurizing system which allows the pressure to be raised up to 50 MPa with an absolute uncertainty of ± 0.1 MPa and a relative error of ± 0.3%.

For measurements, the cell was filled with the polymer and heated up to the required temperature (figure 2a). The spectra were recorded for the neat polymer. CO_2 was then added up to the highest desired pressure (figure 2c). At this pressure, the swelling of the polymer was the most important.
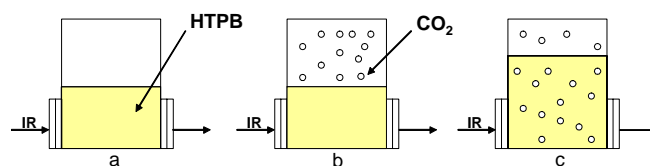
Figure 2. Principle of the HTPB swelling

The system was kept under an isobaric and isothermal condition for few hours. After recording the spectrum, the pressure was decreased to a lower value. For each pressure, the equilibrium was considered to be achieved when no change of the spectral bands was noticed.

Results. IR spectra of HTPB[8] subjected to CO_2 were recorded for a pressure of 15MPa and for 3 temperatures: 40, 100 and 150°C. Using the intensities of a peak centered at 6104 cm^{-1} characteristic of the polymer and a band of CO_2 sorbed in HTPB (combination mode of the CO_2, $\nu_1+2\nu_2+\nu_3$ at 4960 cm^{-1}), it is possible to obtain the swelling of the polymer saturated by supercritical CO_2 and the mass percentage of CO_2 incorporated into the polymer thanks to the following equations.

The concentrations of polymer before (C_0) and after exposure to CO_2 (C) are given by the Beer-Lambert law[6]:

$$A_0 = \varepsilon.C_0.l \qquad (1)$$

$$A = \varepsilon.C.l \qquad (2)$$

If V is the volume of the polymer before exposure to gas and V + ΔV the volume of the polymer during exposure to gas, it is possible to write:

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

The swelling of the polymer is obtained by combining these equations:

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

The concentration of CO_2 incorporated into HTPB (C_{CO2}) is given by the Beer-Lambert law using the integrated absorbance of the $\nu_1 + 2\nu_2 + \nu_3$ band of CO_2 at 4960cm^{-1}. For a comparison with literature data, CO_2 mass sorption incorporated into polymer matrix is given by:

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

where ρ_{pol} is the polymer density ($\rho_{pol} = 0.9$).
Figure 3 shows the variations of HTPB swelling and CO_2 mass sorption at 15MPa for 3 temperatures (40°C, 100°C and 150°C).
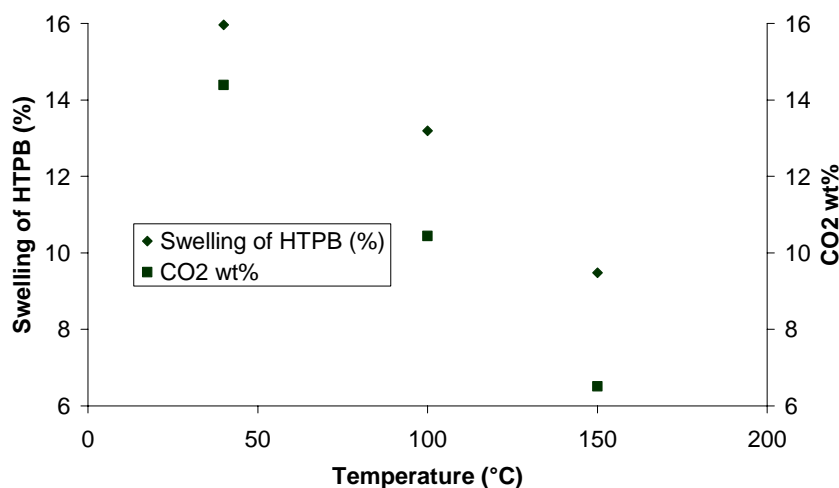
Figure 3. Swelling of HTPB and CO_2 weight percentage at 15MPa for three temperatures

At constant pressure, an increase of temperature causes a decrease of the weight percentage of CO_2 incorporated into the polymer and of the swelling of HTPB what could be explained by a weakening of the CO_2 - polymer interactions : the maximum swelling (16%) and weight percentage of CO_2 (about 14%) are obtained at 40°C - 15MPa. This behaviour is also observed for PolyEthyleneGlycol (PEG)[8,9]. However, the maximum values of PEG swelling (35% at 40°C - 12MPa) and weight percentage of CO_2 (23% at 40°C - 12MPa)[9] are higher than for HTPB. The higher solubility of CO_2 in PEG might be explained by stronger molecular interactions of CO_2 with ether functional group than with C=C double bonds of HTPB.
In addition to the study of the swelling of HTPB by scCO$_2$, viscosity has also been investigated. Indeed, it is an important parameter for the understanding of nucleation and growth phenomena[10].


VISCOSITY OF THE HTPB / CO$_2$ SYSTEM

Description of the viscosimeter. The principle of the falling ball viscosimeter consists in observing the fall of a bead in an open tube immersed in a homogeneous medium (here HTPB + CO_2). Since the tube is open at the bottom and at the top, the fall of the bead acts as a piston and leads to a parabolic velocity distribution in the fluid. The tube diameter is only 100 - 500 nm greater than the bead diameter. The terminal velocity is then small enough to have a short time for attainment of steady state and to have a creeping flow (Re<<1). It can be shown for this geometry that the viscous forces exerted by the fluid on the bead are linked to the overall forces exerted by the fluid on the inner tube surface in the developed expression of the momentum balance. By using the classical correlation for the friction factor (f = 16/Re) for flow in tubes, an estimation of the viscosity can be obtained with the measured terminal falling velocity of the bead. This value has to be corrected by the way of a simulation (thanks

to COMSOL®) or a correlation which takes into account the specific form of the velocity distribution near the bead.

The enclosure containing the viscosimeter is a cylindrical cell (2.6L). The pressure and the temperature can be raised up to respectively 44MPa and 200°C (heating collar). Four sapphire windows allow the lighting of the inside of the enclosure. Thanks to four others and a digital camera, it is possible to detect the fall of the bead. In order to facilitate the cleaning of the enclosure, a glass vessel located in the enclosure contains the polymer solution, an agitator, a bead distributor and a glass tube (figure 4).
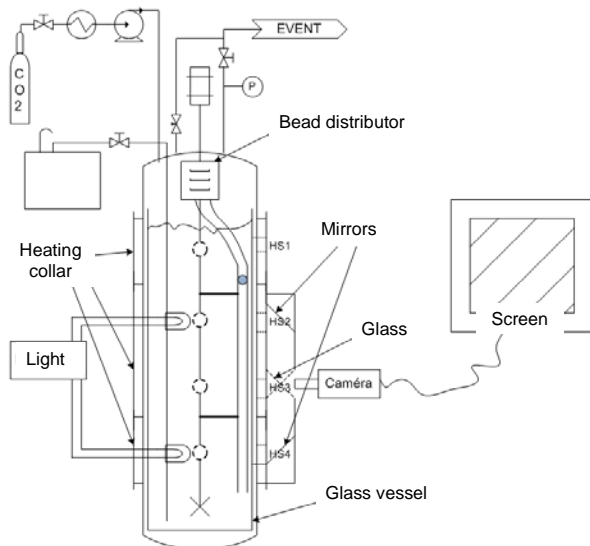
Figure 4. Diagram of the experimental set-up
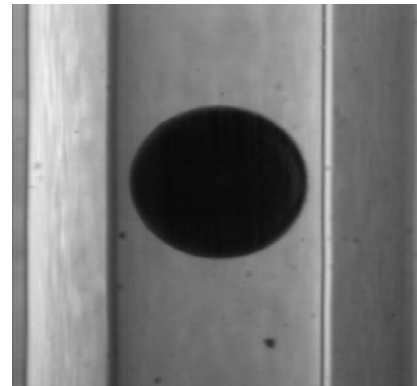
Figure 5. Picture of the fall of a bead

The glass tube is immersed into the polymer and connected to the bead distributor. Its aim is to guide the bead all the long of the enclosure. The tube diameter depends on the diameter of the bead and allows a restricted flow fall of the bead in the fluid (figure 5). Here, the tube has a diameter equal to 8 mm for a diameter of alumina bead of 7.9370 mm ± 0.0006.
The camera is connected to a PC for grabbing pictures. These pictures are then processed by a Matlab® program to deduce the terminal velocity of the bead and then the viscosity of the polymer saturated by $scCO_2$.

In a typical experiment, the glass vessel is filled with the polymer. The enclosure is heated at the desired temperature and CO_2 is added up to a pressure P_1. Agitation allows equilibrium to be reached faster. The mixture is then allowed to rest up to the saturation pressure P_2. The bead distributor is operated and the fall of the bead is recorded thanks to the camera. This step is repeated 5 times to ensure a good reproducibility of the experiment. At the end of the procedure, the mixture is expanded into a container thanks to a plunging tube.
Calculations are in progress to obtain the viscosity of HTPB depending on the CO_2 density. These results will be available for the conference.

# NANOSTRUCTURATION OF HTPB MATRIX WITH COPPER NANOPARTICLES

Experimental procedure. Firstly, the precursor powder (copper (II) acetylacetonate ($Cu(acac)_2$)) is crushed and then mixed with the polymer. The solution is incorporated into the reactor. The system is heated and a CO_2 pressure is applied to obtain decomposition of the precursor in supercritical conditions. The colour of the mixture 'precursor + polymer' turns into red after reduction.

Results. Thanks to i*n situ* UV-Visible spectroscopy we follow the apparition and the evolution of the plasmon band of copper nanoparticles centred at 580 nm[11]. It allows an accurate determination of the decomposition temperature of the precursor through the formation of copper nanoparticles. The saturated band below 400 nm is due to the strong absorption of polymer and metal – ligand bond.
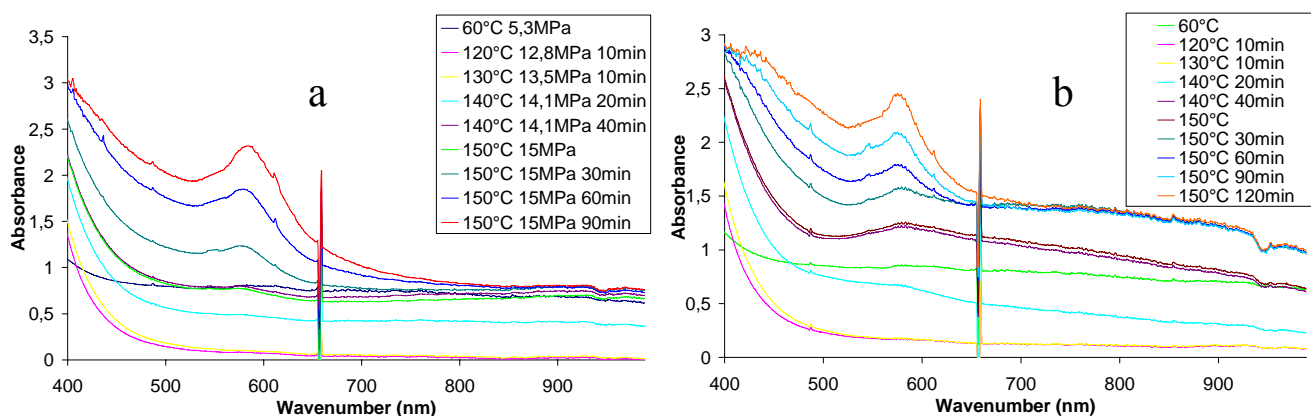
Figure 6. UV – Vis spectra of copper nanoparticles formation with (a) and without CO_2 (b)

Copper (II) acetylacetonate is decomposed at 200°C in $scCO_2$[12]. It appears from this study that in HTPB matrix saturated by $scCO_2$, copper formation occurs at 150°C with or without CO_2. Moreover, CO_2 has an effect on kinetics of copper nanoparticles formation: the absorbance is saturated (or equal to 2.5) after 90 min in presence of CO_2 and after 120 min without CO_2.
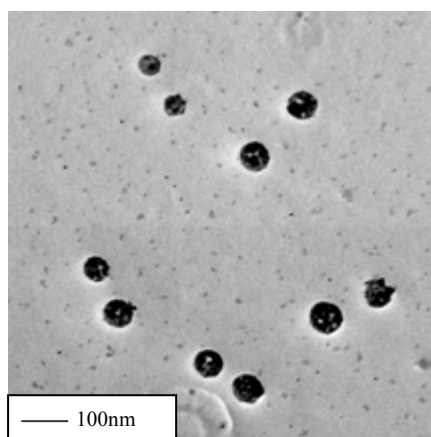
Figure 7. TEM images of copper based nanoparticles in the HTPB matrix

High Resolution Transmission Electron Microscopy shows two kinds of crystalline nanoparticle populations (figure 7): the first, with an average diameter equal to 5nm and 40nm for the second.

CONCLUSIONS

We have reported here a complete method for the optimisation of the synthesis of inorganic nanoparticles in polymer matrixes, especially in this study, copper nanoparticles in HTPB matrix. Thermodynamical behaviour of the polymer / CO_2 system has been studied by IR spectroscopy. We have obtained accurate values of CO_2 mass percentage sorbed in HTPB which is an important parameter for the determination of kinetics of copper nanoparticles formation (as shown by UV spectroscopy).

The study of HTPB viscosity depending on CO_2 density 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. All these parameters give an accurate knowledge of the nanocomposite system in order to optimize the synthesis (size and dispersion) of metal nanoparticles directly in the polymer matrix.

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