SUPERCRITICAL CARBON DIOXIDE, A TOOL FOR POLYMERS SYNTHESIS, NANOCOMPOSITES PREPARATION AND FOAMING

At the time being and for environmental reasons, the use of volatile organic compounds (VOCs) has to be restricted, which makes the search for environmentally compliant polymerization media and systems highly desirable. Presently, attention is paid to the use of supercritical fluids (SCF), especially supercritical carbon dioxide ($scCO_2$), as a potential green solvent. Indeed, $scCO_2$ exhibits low cost (2 $/kg), absence of toxicity, non flammability, easy recyclability and very low critical parameters (P_c = 73.8 bar, T_c = 31.1 °C), compared to others SCF like water (P_c = 372b, T_c = 220°C). Moreover, the solvent strength, i.e. density and polarity of CO_2, can be finely tuned by adjusting the pressure and the temperature which makes it very useful in numerous applications such as supercritical fluid extraction, organic synthesis, homogeneous and supported catalysis, (controlled) polymerizations as well as for polymers processing and nanocomposites preparation.

PART A: POLYMERS SYNTHESIS IN SC CO_2 : DISPERSION ROP OF E-CAPROLACTONE AND DISPERSION ATRP OF VINYL MONOMERS

B. Grignard [1], C. Calberg [1], C. Jérôme [1], W. Wang [2], S. Howdle [2], R. Jérôme [1], C. Detrembleur[1]

[1]*Centre for Education and Research on Macromolecules, University of Liège, Belgium*

[2] *School of Chemistry, University of Nottingham, United Kingdom*

Keywords : ATRP, ROP, dispersion polymerization, living polymer beads

In the field of polymers synthesis, due to the insolubility of most polymers in $scCO_2$ (except non crystalline fluoropolymers and silicones), extensive research has been devoted to the development of heterogeneous processes (dispersion, suspension or emulsion polymerization) mainly by conventional free-radical or uncontrolled polymerization. In order to prepared polymers with well-defined molecular weight, architecture and chain end functionality, dispersion Ring-Opening Polymerization (ROP) of ε-caprolactone (ε-CL) and dispersion Atom Transfer Radical Polymerization (ATRP) of vinyl monomers have been investigated by our group. In case of ROP in dispersion, a series of fluorinated diblock and triblock copolymers of poly(ε-caprolactone) and poly(heptadecafluorodecylacrylate) were prepared by combining ROP of ε-CL and ATRP of the acrylate. These copolymers, with well-controlled molecular weights and compositions, were used as stabilizers for the ROP of ε-CL in $scCO_2$ initiated by tin alkoxide. Effect of composition and architecture of the polymeric stabilizers onto the stabilization of PCL microspheres was investigated.

Controlled dispersion ATRP of MMA was also successfully carried out for the first time in $scCO_2$ in the presence of aminated fluoropolymers, that played the dual role of macroligand for copper bromide and polymeric stabilizer of PMMA microspheres. This catalytic system was also successful in the homogeneous ATRP of 2,2,2-trifluorethyl methacrylate (FMA) in $scCO_2$. Finally, the “one pot” synthesis of well-defined PMMA-b-PFMA diblock was also considered using a special high pressure vessel allowing injection of monomers under pressure. At the end of the polymerization, the diblock copolymer was collected as small size microspheres attesting for the living character of the polymerization during the preparation of the PMMA beads.

PART B : POLYMER/CLAY NANOCOMPOSITES PREPARATION

In the two last decades, a great deal of attention has been focused on developing reinforced materials with incorporation of nanometric fillers. Amongst the different types of nanofillers, those based on layered silicates (commonly known as clays), and more especially natural montmorillonite (MMT), have been most widely investigated. Compared to more classical "microfillers", only a small quantity of MMT is needed to enhance several properties such as gas permeability, fire resistance and mechanical properties. However, the nanocomposite performances are strongly dependent upon the clay dispersion. The challenge is thus to achieve a good delamination of the MMT nanolayers in order to obtain sheets totally independent one from each other. For that reason, the Na^+ cations lying in the clay interlayer galleries are usually exchanged with organic cations bearing a long hydrocarbon chain (C_{12}-C_{18}) in order to improve the compatibility with the polymers. This exchange is well known in water due to its capacity of swelling of the clay. However, this solvent strongly limits the range of surfactants used.

PRODUCTION OF HIGHLY EFFICIENT NANOCLAYS IN SUPERCRITICAL CARBON DIOXIDE

E. Naveau, L. Urbanczyk, C. Calberg, R. Jérôme
1Centre for Education and Research on Macromolecules, University of Liège, Belgium

Keywords : nanocomposites, organoclays, phosphoniums salts, supercritical carbon dioxide

In order to enlarge the variety of organo-modifiers, supercritical carbon dioxide has appeared to be a very interesting solvent, due to its excellent transport properties [1]. The process is simple, environmentally friendly and easy to transfer to the industrial scale. Indeed, typical conditions for the exchange reaction in $scCO_2$ are a temperature of 40°C, a pressure of 100 bars for 2 hours. Moreover, after reaction and depressurization, no elimination of solvent is required as dried clays are directly obtained. Using this process, three types of nanoclays have been prepared : fluorinated nanoclays, siliconated nanoclays and high temperature stable nanoclays. These last phosphonium-modified clays, stable up to 260°C, are particularly interesting for melt processing of polymers above 180°C such as PC, PE, PP and aromatic PA. Kilograms of these organoclays may now be produced thanks to our laboratory's pilot plant.

Reference

[1] Stassin, F.; Calberg, C.; Jérôme, R., *PCT Int. Appl.* **2004**, WO 2004/108805

USE OF SUPERCRITICAL CARBON DIOXIDE FOR POLYMER/CLAY NANOCOMPOSITES PREPARATION AND FOAMING

L. Urbanczyk, F. Stassin, C. Calberg, R. Jérôme
[1]*Centre for Education and Research on Macromolecules, University of Liège, Belgium*

Keywords : supercritical fluid, nanocomposite, clay, masterbatch, ring-opening polymerization, polycaprolactone, foam

There are different ways to produce polymer/clay nanocomposites but melt intercalation is the preferred method in industry due to the flexibility of the process and cost reasons. However, even with organomodified clays, a complete exfoliation is only achieved by this way in a few cases.

In order to improve the clay dispersion via the melt blending technique, a highly charged polymer/clay nanocomposite ($>30\%_{wt}$) is prepared by *in situ* polymerization of ε-caprolactone. The polymer lies between the clay sheets and increases the clay interlayer spacing, leading to a pre-exfoliated clay, also called masterbatch. This synthesis has been successfully conducted in $scCO_2$ for its environmental friendliness but also because the product is recovered as a dry fine powder, avoiding expensive drying and grinding steps.

A superior clay delamination has been achieved after melt dispersion of PCL/clay masterbatches into poly(styrene-co-acrylonitrile) (SAN) compared to the direct melt blending of the original clay. This is explained by the better compatibility between SAN and the clay interface covered by PCL, which is miscible with SAN.

Polymer/clay nanocomposite foams have drawn a lot of attention mainly due to their excellent strength-to-weight ratio, good thermal insulation, materials savings, etc. Supercritical CO_2 has been used as a physical foaming agent, for the foaming of PU/clay nanocomposites. The nanocomposite foam shows a fine microcellular structure with a smaller cell size than the neat PU foam, and enhanced Young’s modulus during compression tests.