

ABSTRACT

Polymer nanocomposites are new plastic materials reinforced by inorganic fillers at the nanometric scale. Among the fillers, clay minerals are particularly attractive because of their natural occurrence and the high surface/volume ratio of their constituting layers. A small amount of clay sheets dispersed in a polymer matrix can greatly improve properties such as mechanical, thermal, gas barrier and flame-retardancy properties. However, as clays are hydrophilic by nature and present a poor compatibility with most polymers, a surface modification is often required to ensure a good dispersion of the nanosheets.

This thesis deals with the preparation of new organoclays for polymer nanocomposite applications. To enlarge the range of used organic modifiers, carbon dioxide (CO₂) in its supercritical state (above 31°C and 74 bar) is proposed as a green medium for the clay modification. Indeed, this environmentally benign, inexpensive and non-flammable solvent possesses the required high diffusivity to facilitate the penetration of organic molecules inside the clay layers. Moreover, as CO₂ is a gas at ambient conditions, a simple depressurization leaves a dry, ready-to-use organomodified clay powder.

In this work, we demonstrate the versatility of the supercritical CO₂ (scCO₂) process through the preparation of thermally stable organoclays and functional organoclays, and their evaluation as nanofillers in polymer matrices.

We first illustrate that ionic exchange in scCO₂ is driven by the formation of insoluble inorganic salt issued from the combination of clay sodium cation and counterion of ammonium, phosphonium or imidazolium organomodifier. Then, the influence of onium stability on morphology and fire properties of polyamide-6 nanocomposites is evaluated. With the same degree of dispersion and the same alkyl substituents, ignition times were longer with phosphonium-modified clays than with ammonium-based clays. In comparison with a commercial organoclay, scCO₂-prepared phosphonium clay showed a larger extent of exfoliation and larger reinforcement in polyamide-6, whereas undesirable higher oxygen permeability is measured in poly(*m*-xylylene adipamide). Finally, functional organoclays were used for the *in situ* polymerization of methyl methacrylate in scCO₂ via two radical pathways: a conventional free radical polymerization and a controlled radical process (Atom Transfer Radical Polymerization). Polymer microspheres are obtained with poly(dimethylsiloxane)-modified clays or when a fluorinated stabilizer is added to the polymerization, demonstrating the convenience of this environmentally friendly process.