PREPARATION OF SPECIALTY NANOCLAYS IN SUPERCRITICAL CARBON DIOXIDE

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Due to their exceptional mechanical and barrier properties, layered silicate nanocomposites find an increasing number of applications in the automotive and the packaging industry[1]. However, the commercial nanoclays used in this new generation of plastics, suffer from a poor thermal stability. Indeed, the ammonium surfactants present at the surface of the clay undergo a rapid degradation as early as 180°C, i.e., the lower temperature limit for melt processing of many polymers[2]. In order to enlarge the range of organoclays available, our lab is using supercritical CO_2 as a solvent for the modification of natural clays[3]. This environmentally friendly process enables us to use non water-soluble phosphonium salts and requires no drying of the clay.

In this work, we intercalated different highly stable phosphonium salts such as trihexyltetradecylphosphonium chloride (P14), hydroxyethyl triphenylphosphonium bromide (P-OH) or carboxybutyl triphenyl phosphonium bromide (P-COOH) in natural clays (MMT). Typical conditions for the exchange reaction in sc CO_2 were a temperature of 40°C and a pressure of 100 bars, during 2 hours. These conditions are particularly interesting compared to those used in classical solvents, usually 80°C and 24 hours.

In some cases, the addition of 2 % vol. of a co-solvent was necessary for a successful ionic exchange. The influence of the structure of the cation, the nature of the counter ion and the polarity of the co-solvent was studied. The interlayer distance was determined by X-ray diffraction (Fig. 1). It is proportional to the size of the cation and lies between 1.4 and 2.7 nm. The thermal stability evaluated by TGA was up to 280°C.

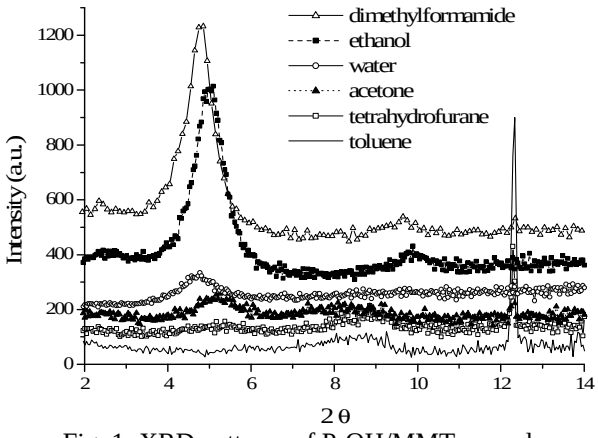

Fig. 1: XRD patterns of P-OH/MMT nanoclays obtained in sc CO_2 with different co-solvents

The phosphonium-modified clays were melt blended with poly(vinyl chloride), polyamide 6 and maleic anhydride-grafted polypropylene at temperatures between 180°C and 250°C with a 3 wt% clay content, leading to intercalated/exfoliated nanocomposites.

Finally, this process can be extended to obtain highly fluorinated nanoclays for the preparation of nanocomposites based on poly(vinylidene difluoride) or other fluorinated matrices.

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