

SYNTHESIS OF PCL/CLAY MASTERBATCHES IN SUPERCRITICAL CARBON DIOXIDE AND THEIR REDISPERSION INTO POLY(STYRENE-CO-ACRYLONITRILE).

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Recently, 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, and especially the natural montmorillonite, have been most widely investigated. Compared to more classical charges, only a small quantity of nanofiller is needed to enhance several properties such as gas permeability, fire resistance and mechanical properties [1]. This difference is due to the higher specific surface of the nanometric fillers.

The challenge is to achieve a good delamination of the clay into the polymer in order to obtain silicate sheets totally independent from each other. There are two common ways to prepare polymer/clay nanocomposites : melt intercalation and in-situ polymerization. In this poster, we present a combination of the two methods that gives rise to an excellent exfoliation of the clay. This is called the masterbatch process [2].

This process is based on the preparation of a pre-exfoliated clay by in-situ polymerization of ϵ -caprolactone [3] in the presence of an organomodified clay (Cloisite[®] 30B) in $scCO_2$ (figure 1). This masterbatch is then redispersed in the poly(styrene-co-acrylonitrile) (SAN) matrix by melt blending.

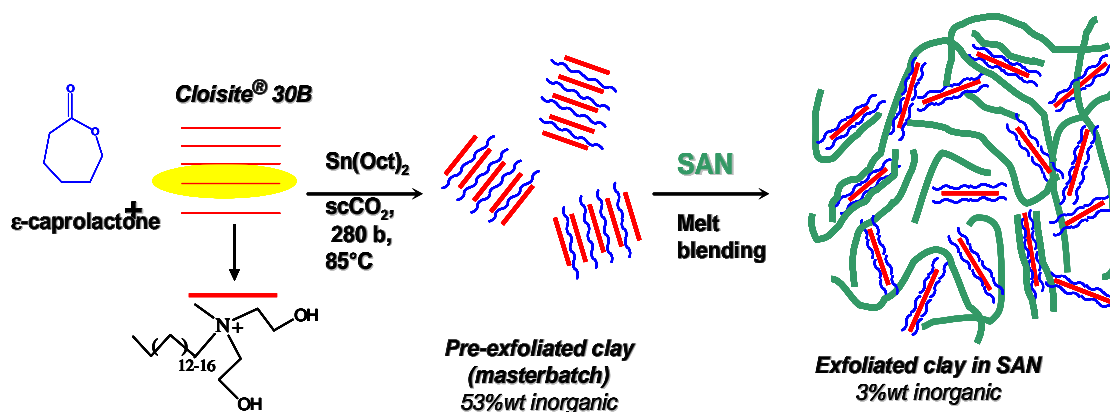


Figure 1. Scheme of the strategy used to obtain a good exfoliation of an organomodified clay into a polymer matrix.

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The advantages of using supercritical carbon dioxide as a polymerization medium are multiple : this gas is environmentally friendly, non-toxic, the critical parameters are easily attainable ($T_c=31,1^\circ\text{C}$, $P_c=73,8\text{b}$) and the product obtained after depressurization is a dry fine powder, which avoids an expensive step of drying. Furthermore, masterbatches with a high clay loading ($>50\%$ wt inorganic part) can be synthesized without any viscosity problems, which is not the case in a more conventional medium, such as in toluene or even in the bulk. A pilot unit of 50L is now available and under current use for the production of up to 20kg of polycaprolactone (PCL)/clay masterbatches at once in scCO_2 .

The pre-exfoliation of the clay in the masterbatch (53%wt) has been confirmed by XRD analysis, where the interlayer distance of the organomodified clay increased from 1,8nm in Cloisite[®]30B to 3,3nm in the masterbatch. This proved the intercalation of the polymer chains between the clay sheets.

The final SAN/clay nanocomposites have been directly observed by transmission electron microscopy (figure 2). The quality of clay dispersion of the PCL/clay masterbatch into the SAN has been compared with the direct melt blending of the commercial clay. It clearly appears that some big stacks remained with the direct melt blending process whereas an homogeneously exfoliated nanocomposite was obtained with the masterbatch route.

The enhanced delamination efficiency of the masterbatch is attributed to the better penetration of the SAN chains between the clay layers thanks to the affinity between the PCL and the SAN.

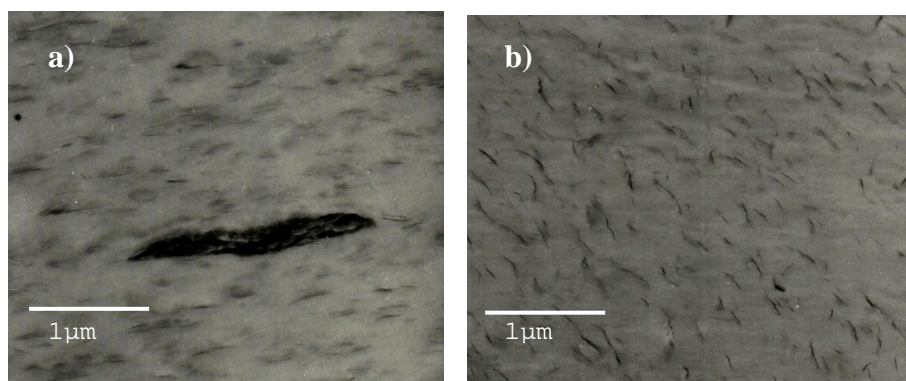


Figure 2. TEM Micrographs of SAN filled with 3% wt Cloisite[®]30B via a) direct melt blending and b) the PCL/clay masterbatch redispersion.

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