



	Experiment title: SAXS measurement of waterborne polymer/clay nanocomposites.	Experiment number: 16-02-35
Beamline: BM16	Date of experiment: from: 07/02/08 to: 10/02/08	Date of report: 09/09/08
Shifts: 9	Local contact(s): Dr. Francois FAUTH	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Ms. Audrey Bonnefond*, Dr. Jose Ramon Leiza*, Dr. Maria Paulis* Universidad del País Vasco / Euskal Herriko Unibertsitatea Joxe Mari Korta Zentroa Avda. Tolosa, 72 20018 Donostia-San Sebastián Spain		

Report:

The inclusion of small amounts of clay to polymeric materials has produced the enhancement of several materials properties such as increased heat resistance, increased strength or decreased gas permeability. However the beneficial effect of the clays is most observed when the clay is exfoliated inside the polymer matrix. The main method to observe such exfoliation is by TEM of the cryo-ultramicrotomed samples. However TEM observations do not provide an average spacing between clay layers in the material. That interlayer space could be measured by WAXD, but the technique is only able to be sensible above 2° or around 4nm of interlayer space. Therefore new techniques, as can be the SAXS, are required to effectively determine the barrier between intercalated and exfoliated clays.

In previous stays at BM 16 beam line, the presence of a scattering peak at $q=1.65\text{nm}^{-1}$ attributed too the SLS emulsifier (sodium lauryl sulfate) was proved, the swelling of commercial orgnophilic clays with MMA/BA monomers was measured and the appearance of fringes in the in–line emulsion polymerization of polymer/clay hybrids was seen. These in-line emulsions were not carried out in properly agitated vessels. Therefore the main task of this stay has been the use of an in-house made jacketed reactor with agitation possibility, in order to mimic more precisely the reaction conditions (see Figure 1). Apart from these on-line measurements, swelling studies of Cloisite 30B with different monomers were also performed and physical mixtures of a blank latex with clay have also been measured by SAXS.

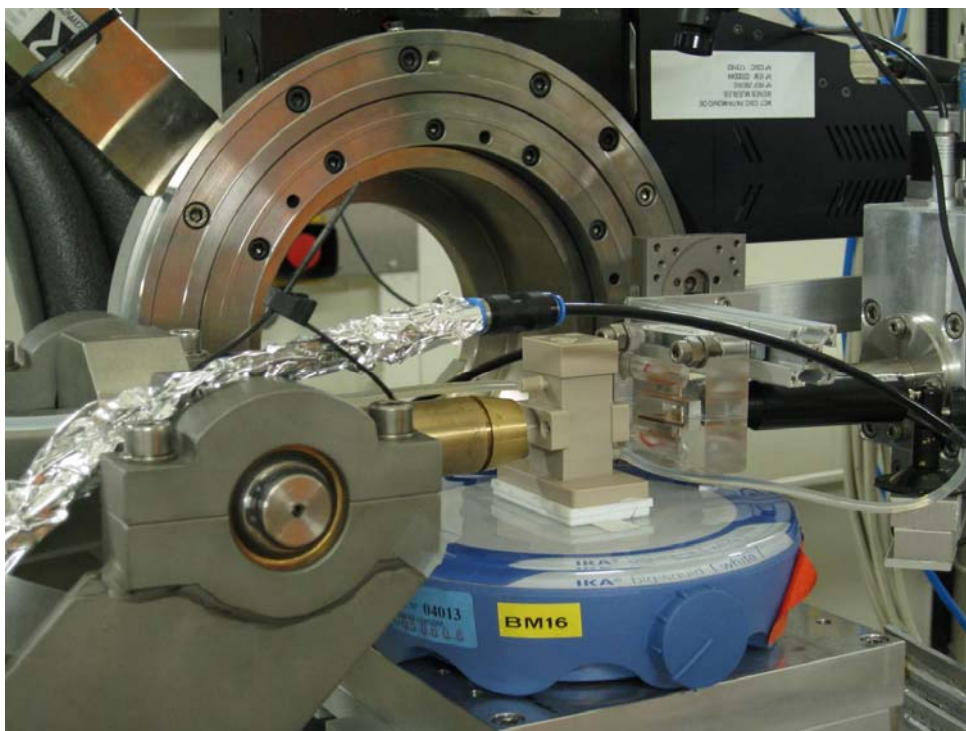


Figure 1. Equipment used to perform in-situ miniemulsion polymerization measurements.

Small-angle X-ray scattering (SAXS) measurements were carried at the Spanish CRG beamline BM16 in the European Synchrotron Radiation Facility in Grenoble, with the technical aid of Dr. Francois Fauth. Two different wavelength of the monochromatic X-ray beam were used: $\lambda=1.387\text{\AA}$ and 0.726\AA . The equipment was aligned at two different sample-to-detector distances: 2.4m and 5.4m, respectively. A 2-D detector marCCD165 was used and the signal was treated (corrected for background) and converted to 1D through a Fit2D software. The scattering angle was calibrated by a silver behenate standard.

This time mainly liquid like samples were measured in two types of sample holders: static one (clay aqueous and monomer dispersions, physical mixtures of latexes) and the agitated and jacketed reactor (on-line reaction measurements).

i) SAXS measurements of Cloisite 30B dispersed in different monomers.

Figure 2 shows the SAXS profiles of the Cloisite 30B hydrophobic clay dispersed in MMA, BA and a 50/50 mixture of MMA/BA. As it can be seen, the clay layers are more apart in the presence of BA and less in the presence of MMA. It seems proven that the longer hydrophobic tail of the BA interacts more favourably with the Cloisite 30B modifier, pushing the clay layers more apart.

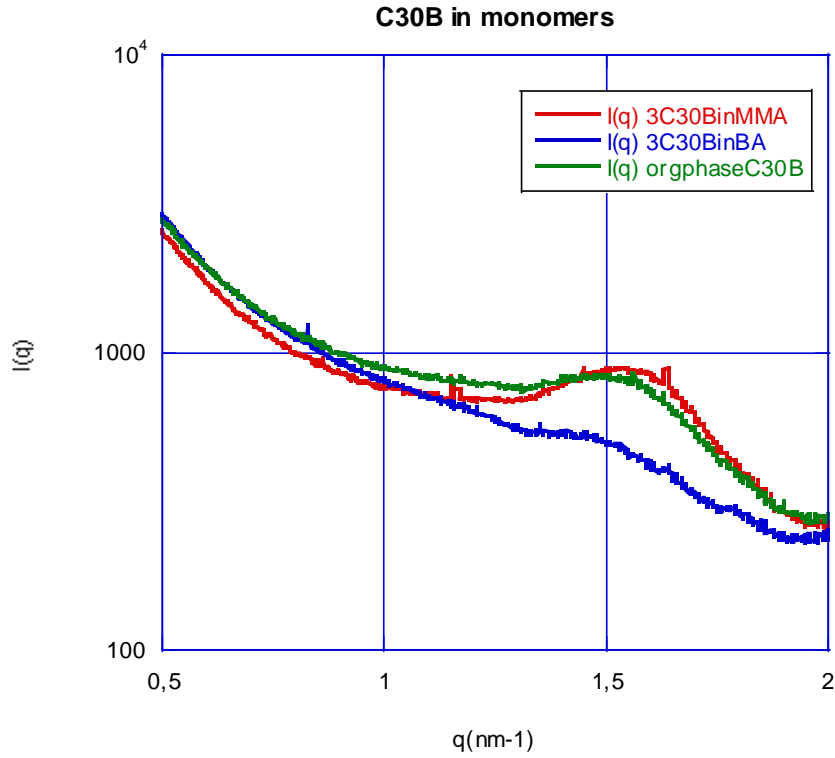


Figure 2. SAXS profiles of Cloisite30B dispersed in different monomers.

ii) SAXS measurements of physical mixtures of blank latexes with Na-MMT clay.

In our last experiments in the BM16, it was concluded that the hybrid polymer/clay latexes synthesised in-situ with organophilic clays possessed the clay on the polymer particles, as the fringes in the scattering profiles were much attenuated when the clay was present. This time, another way to prove this theory was checked. Hydrophilic Na-MMT was physically added to a blank latex (RSC39, synthesised without clay). This hydrophilic clay will remain in the water phase, out of polymer particles contact. Figure 3 presents the scattering profiles obtained from these physical mixtures.

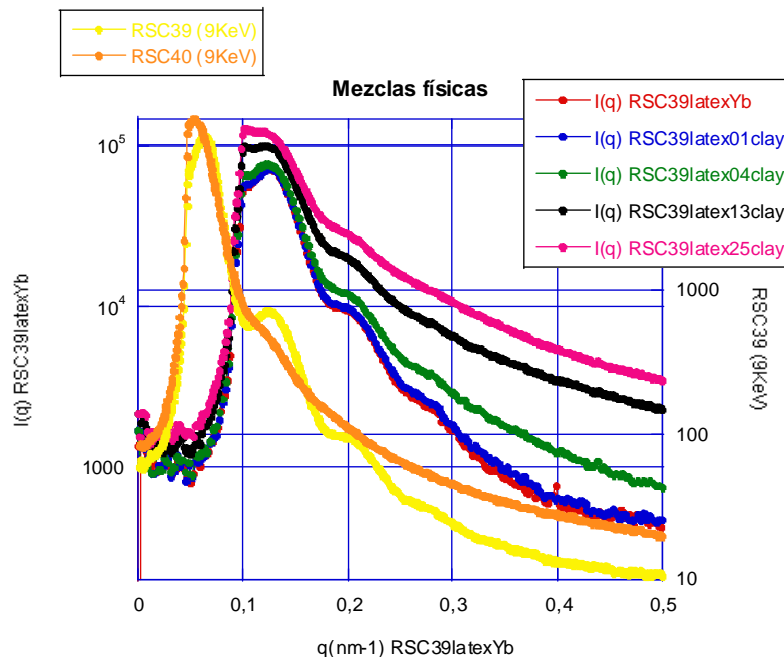


Figure 3. SAXS measurements of physical mixtures of a blank latex (RSC39) with different clay contents, compared to a latex synthesized in situ with clay (RSC40).

As it can be seen, in the physical mixtures, the fringes are much less attenuated than in the latex synthesized with clay (RSC40). We conclude that in the physical mixtures the clay is mainly located in the water phase and in RSC40 on the polymer particles.

iii) In-situ SAXS measurements of miniemulsion polymerization in the presence and absence of Cloisite 30B.

Figures 4 and 6 present the measurements taken on-line from the miniemulsion polymerization of MMA/BA/SA (30% S.C.) with KPS in the absence and presence of Cloisite 30B.

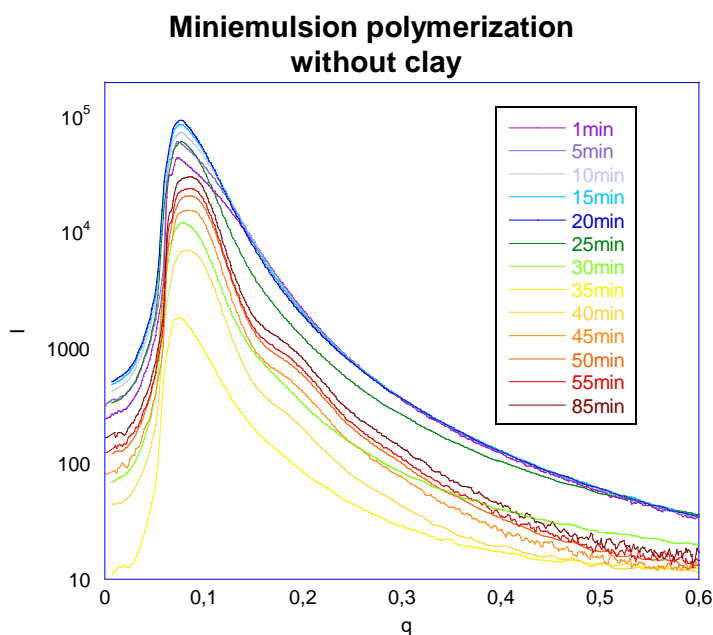


Figure 4. SAXS data of on-line miniemulsion polymerization without clay.

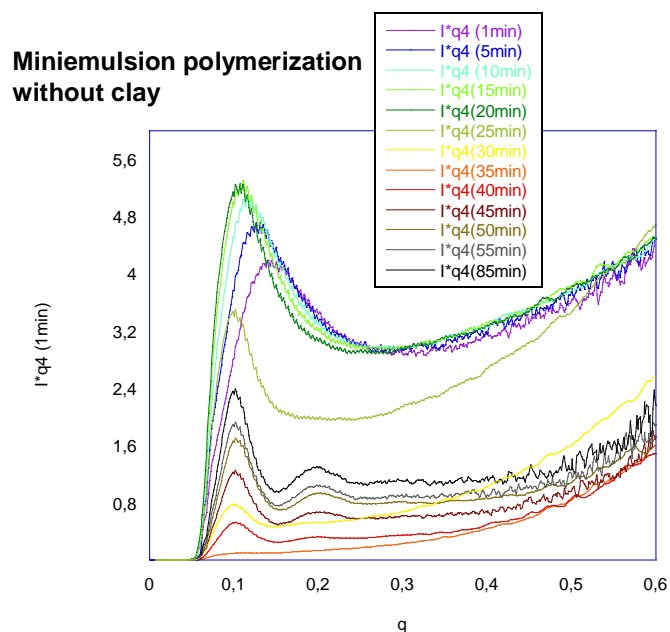


Figure 5. $I \cdot q^4$ vs q plots of on-line miniemulsion polymerization without clay

From these data we infer that particles with diameters of 63nm appear at 40 minutes of reaction, and their size is not varied until the end of the reaction.

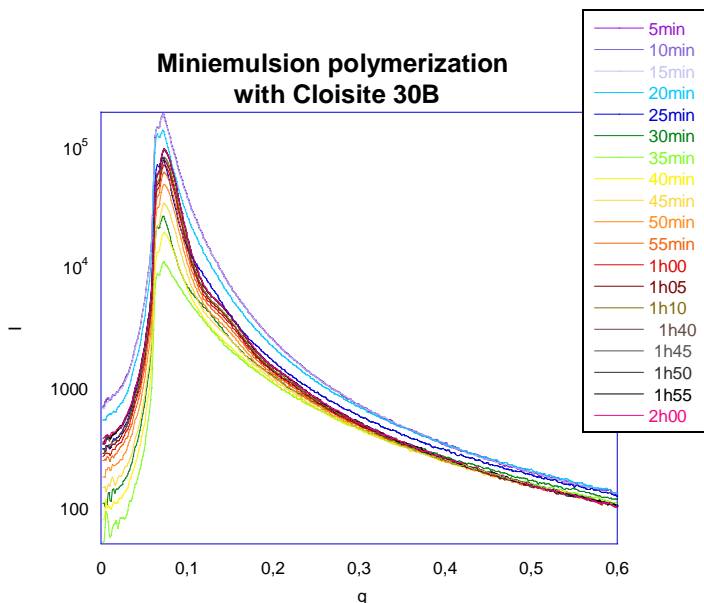


Figure 6. SAXS data of on-line miniemulsion polymerization in the presence of C30B.

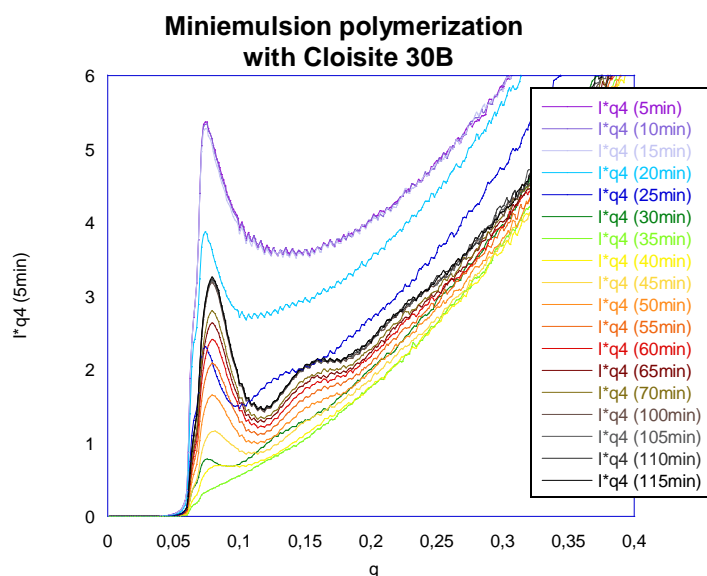


Figure 7. $I \cdot q^4$ vs q plots of on-line miniemulsion polymerization in the presence of C30B.

When the clay is present in the droplets at the beginning of the reaction, a bit different trend is observed in the SAXS spectra of the reaction evolution. At 25 minutes, 107nm particles appear, at 30 minutes they seem to be 126 nm wide, at 35 and 40 minutes we do not see fringes in the spectra and from 45 minutes on, the particles are 86nm wide.

This behaviour was unexpected for us and it should be further studied in next visits to BM16.