ESRF	**Experiment title:** SAXS measurement of waterborne polymer/clay nanocomposites.	**Experiment number**: 16-02-54
Beamline: BM16	**Date of experiment**: from: 14/11/08 to: 17/11/08	**Date of report**: 24/04/09 *Received at ESRF:*
Shifts: 9	**Local contact(s)**: Dr. Francois FAUTH	

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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 2º 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 swelling of commercial organophilic clays with MMA/BA monomers was measured, two miniemulsion polymerization reactions were carried and monitored in-situ using an in-house made jacketed reactor with agitation possibility, in order to mimic more precisely the reaction conditions (see Figure 1), and the appearance of different fringes during polymerization was seen in the presence or absence of clay. Apart from these on-line measurements, physical mixtures of a blank latex with clay were also been measured by SAXS. This time, new measurements have been done with in-house modified MA16-MMT, in order to see if its swelling capacity in monomers differs that of commercial Cloisite 30B, and newly formed latexes (with less emulsifier amount) have been tested in the liquid state.

Furthermore, a new reactor (with easier cleaning device) for in-line measurements has been tried (see figure 2).

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

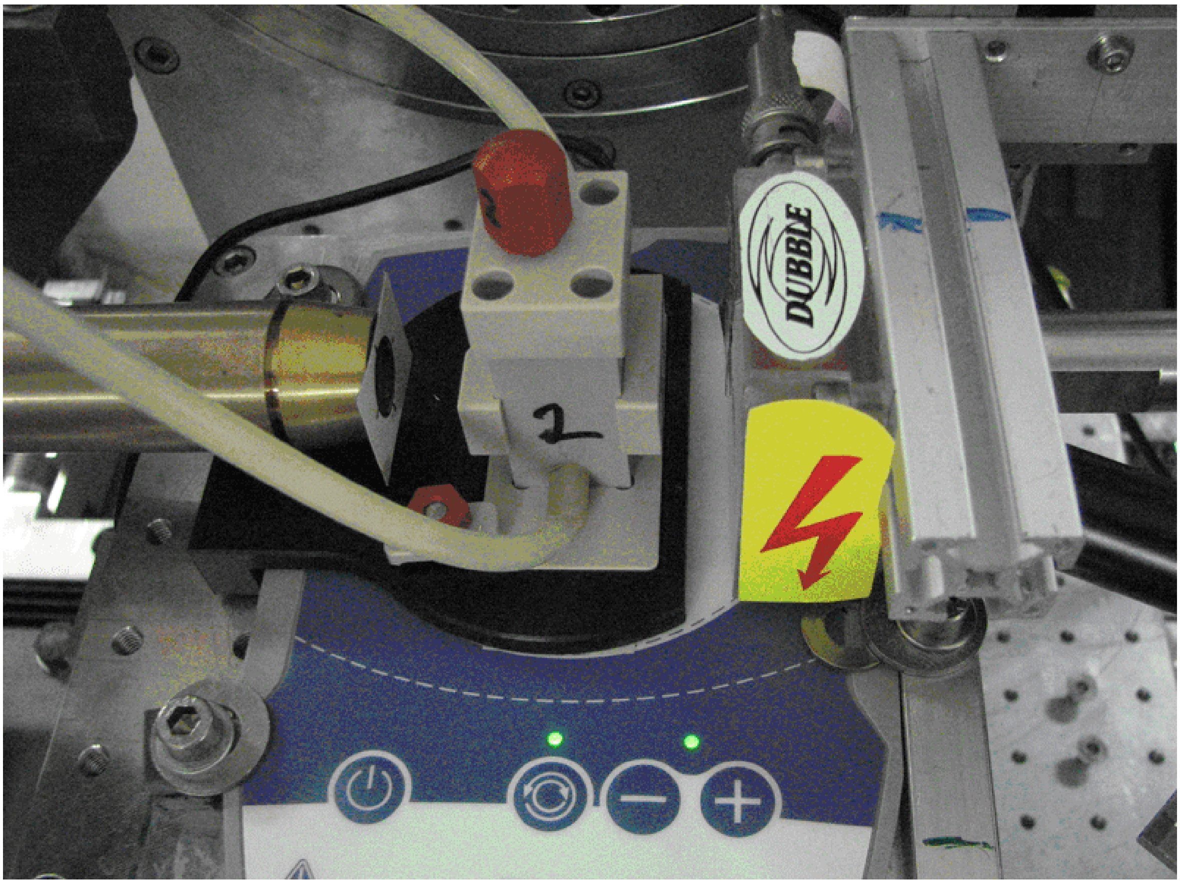


Figure 2. The new equipment used to perform in-situ miniemulsion polymerization measurements.

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. One wavelength of the monochromatic X-ray beam was used: λ=0.9795Å (12.6578KeV, Se_K edge). The equipment was aligned at two different sample-to-detector distances: 6m and 3.52m, 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 (monomer dispersions) and the agitated and jacketed reactor (on-line reaction measurements).

i) SAXS measurements of Cloisite 30B and MA16 modified clay dispersed in different monomers.

Figure 3 shows the SAXS profiles of the Cloisite 30B hydrophobic clay dispersed in a 10/90 mixture of MMA/BA. It was found that the dispersion of C30B in omonomers settled after some time and it was stable if it was sonicated. Therefore we made measurements of the dispersion just performed, of the upper (clear) and lower part after sedimentation, and of the sonified and stable dispersion. It was seen that no great difference was observed in the interlayer space of the clay between the three methods.

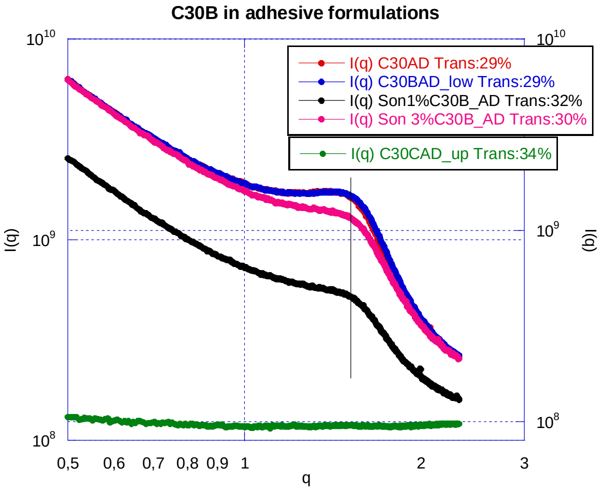
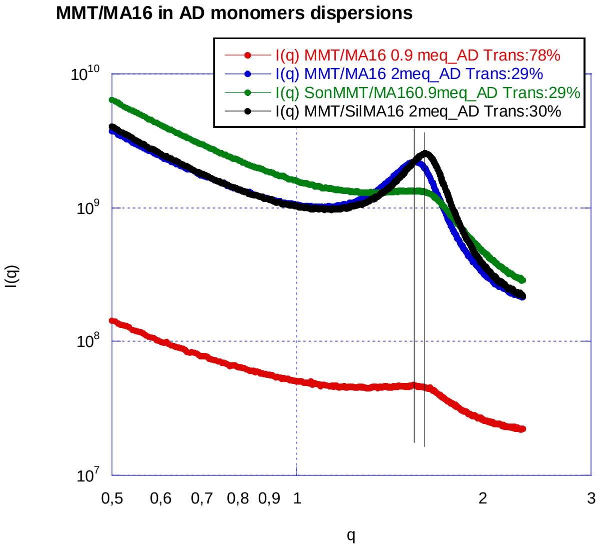


Figure 3. SAXS profiles of Cloisite30B dispersed in monomers with different pretreatments.

The in-house MA16 modified MMT was also dispersed in monomers to check if it was also swollen by monomers. Figure 4 shows that the interlayer space increases from the dry state to the swollen state, and that the clay exchanged with 2meq of MA16 swells more monomers than the one exchanged with 0.9 meq. On the other hand, the miniemulsion performed with the 2meq MA16/MMT presented again the characteristic peak of the clay, suggesting a possible particle inside location of the clay, compared to the surface location of Cloisite 30B.



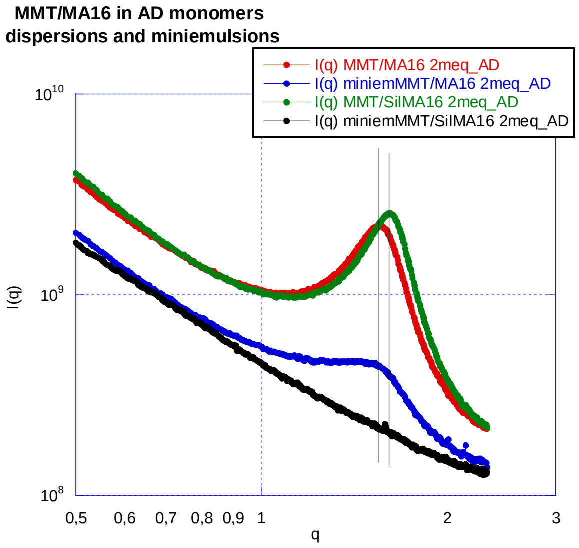


Figure 4. SAXS profiles of MMT modified with different miliequivalents of MA16 and dispersed in monomers with different pretreatments.

Figure 5. SAXS profiles of MMT modified with 2 meq of MA16 and with sililated agents and dispersed in monomers and their miniemulsions.

ii) SAXS measurements of latexes with C30B clay, with lower emulsifier amount.

In our previous experiments in the BM16, it was concluded that the hybrid polymer/clay latexes synthetised in-situ with organophilic clays possesed the clay on the polymer particles, as the fringes in the scattering profiles were much attenuated when the clay was present. Nevertheless, the secondary nucleation produced due to the excess of surfactant in the previous reactions was considered to be responsible for the attenuated fringes appearing in those samples. Lately we have managed to decrease the emulsifier amount of our latexes, in order to avoid secondary nucleation that would geve particles without clay. Figure 6 shows that in the presence of lower amount of emulsifiers, the fringes completely disappear, suggesting clay surface location on most polymer particles.

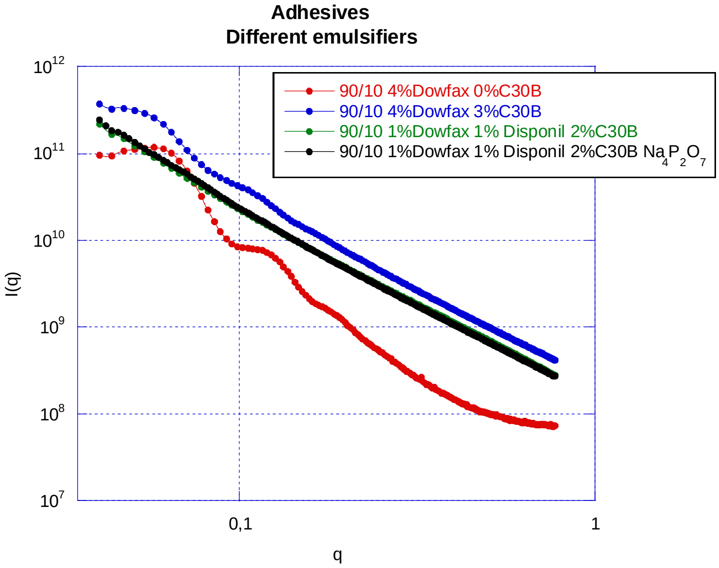


Figure 6. SAXS measurements of latexes with different emulsifier contents.

iii) In-situ SAXS measurements of miniemulsion polymerization in the presence of MA16 modified MMT.

Figures 7 and 8 present the measurements taken on-line from the miniemulsion polymerization of MMA/BA/SA (30%S.C.) with AIBN in the presence of MA16/MMT.

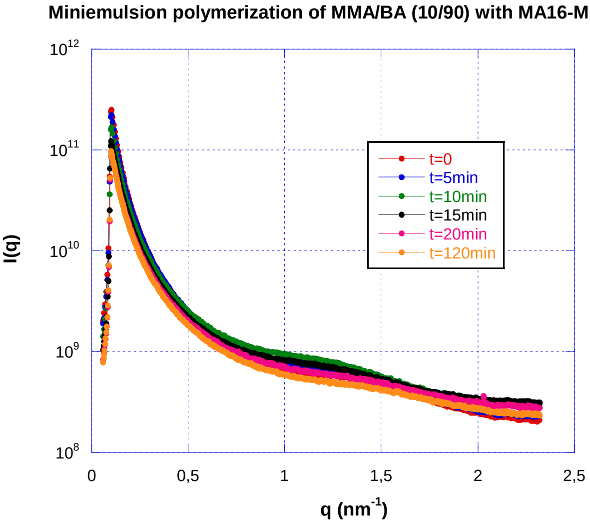


Figure 7. SAXS data of on-line miniemulsion polymerization with MA16/MMT.

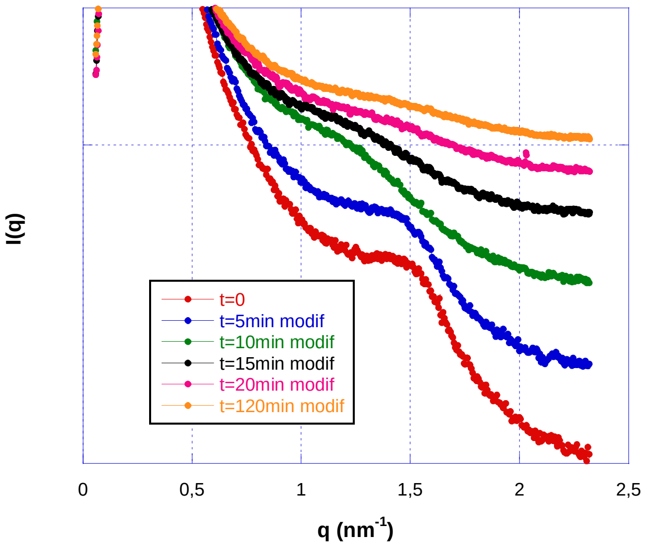


Figure 8. Magnification of the SAXS data of on-line miniemulsion polymerization with MA16/MMT

As it can be observed, no fringes appear in the spectra, due to the low emulsifier amount used in this case (1% Dowfax+1%Disponil), as explained before. However, it can be seen that the clay interlayer space starts expanding as soon as the reactions begins to take place, indicating interlayer polymerization.