	Experiment title: SAXS measurement of waterborne polymer/clay nanocomposites.	**Experiment number**: 16-02-28
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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 WAXS, are required to effectively determine the barrier between intercalated and exfoliated clays.

In a previous stay at BM 16 beam line, analyzing a serie of waterborne poly(MMA-co-BA)/clay nanocomposite films could be observed the presence of a scattering peak at $q=1.65nm^{-1}$. This peak was attributed to the presence of the emulsifier SLS (sodium lauryl sulfate) used our system. Therefore, the goal of research stay was to clarify the average clay interlayer distance of the nanocomposites of the different samples: both solid (nanocomposite films casted from the latex) and liquid (nanocomposite latexes) forms, and to get to know where the clay is located during the polymerization step.

To achieved this, differents issues were followed in our research:

i) A depeer study of the nanocomposite films thoroughly rinsed with distilled water in order to get rid of the SLS fraction migrated to film surface during the film formation.

ii) Different Na-MMT aqueous dispersions and Cloisite 30B monomers dispersions were study in order to calculate the basal interlayer space of the clays.

iii) Two polymerization reactions (emulsion and miniemulsion polymerizations) were monitored on-line, in order to see the evolution of the clay platelets during the polymerization process.

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. Three different wave length of the monochromatic X-ray beam were used: λ=1.387Å, 0.725Å and 0.979Å, respectively. The equipment was aligned at two different sample-to-detector distances: 2.4m and 3.29m, 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.

Two sample types were measured: solid (nanocomposite polymer films) and liquids samples (clay aqueous and monomer dispersions; and liquid nanocomposite latexes).

i)   SAXS measurements of polymer nanocomposite latex films.

For all the polymer nanocomposites latex rinsed films, a peak at q=1.6nm^{-1} was observed in SAXS profiles. Figure 1 shows the SAXS profiles of the nanocomposite latex films prepared by in situ miniemulsion polymerization with different clay content from 2% to 4%, together with a blank latex film where no clay was added (sample S0). This peak was attributed to the crystalline structure of the free SLS fraction that migrated to surface during the film formation.
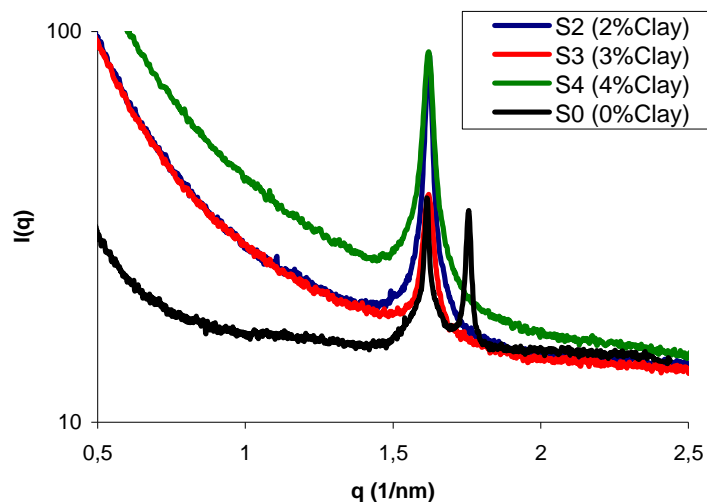
Figure 1. SAXS profiles of nanocomposite latex films with different clay content up to 4wt%.
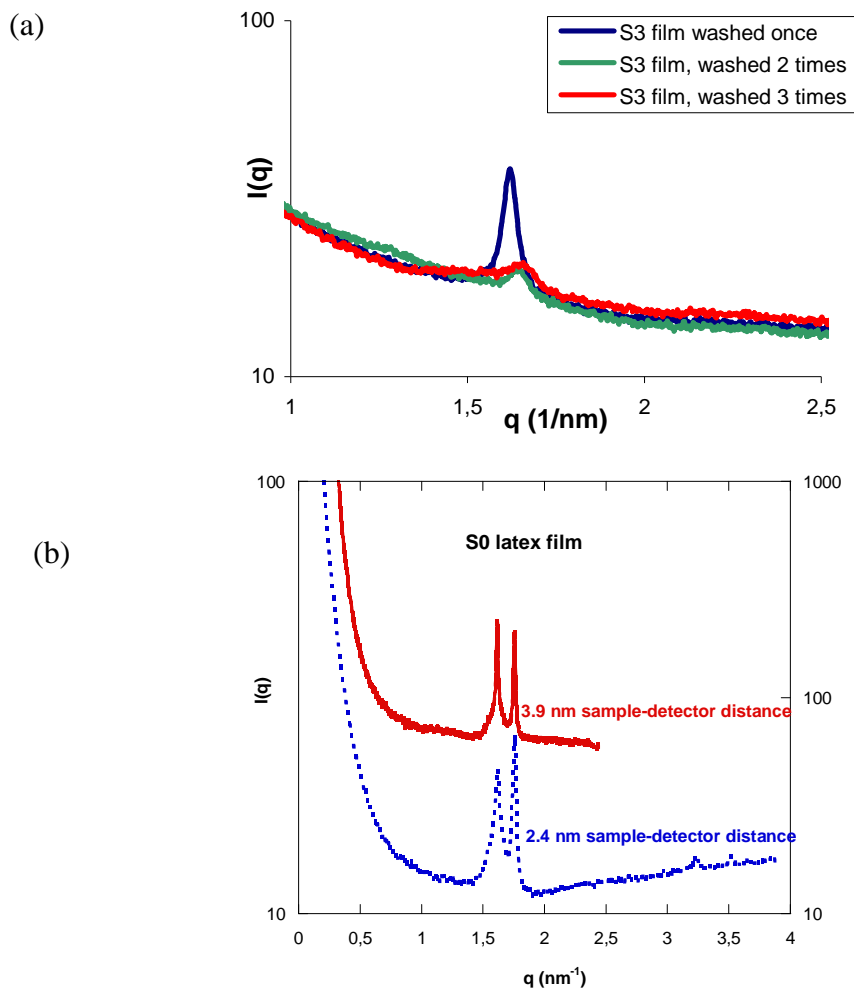
Figure 2. SAXS profiles of nanocomposite latex film (a) that was rinsed several time, (b) at different sample-to-detector distance.

The film S3 that was rinsed several times with distilled water for a thoroughly get rid of SLS and its SAXS patterns are presented in Figure 2a. It can be noticed the scattering peak from $q=1.62nm^{-1}$ still appeared (contrary with what we expected), nevertheless the intensity deceased as the number of rinsing increased indicating that more SLS fraction was removed but could not be completely removed.

The crystalline structure of SLS shows the first and second scattering peaks at $q= 1.6nm^{-1}$ and $q=3.2nm^{-1}$, respectively. The SAXS profiles for the S0 latex film at two different sample-to-detector distances are presented in Figure 2b, and it can be observed that both first ($q=1.6nm^{-1}$) and second ($q=3.2nm^{-1}$) order scattering peaks of SLS appeared. This confirm that the presence of the peak at $q=1.6nm^{-1}$ in all the nanocomposite latex films is due to the crystalline structure of the emulsifier (SLS) used in the formulation.

ii) SAXS measurements of Na-MMT aqueous dispersions.

Various Na-MMT aqueous dispersions were analyzed by the small-angle X-ray scattering (SAXS) technique. Figure 3a presents the scattering profiles of 1% to 4% Na-MMT aqueous dispersions. The scattering intensity, I(q), decayed with increasing the scattering vector, *q*, this behavior being typical of thin-layer particles scattering. It can also be noticed that increasing the clay content, the scattering intensity increased.

The absence of peaks in the SAXS profiles indicated that the clay was swollen with water and that the preferential agglomeration of platelets in stacks was lost when being dispersed in water.
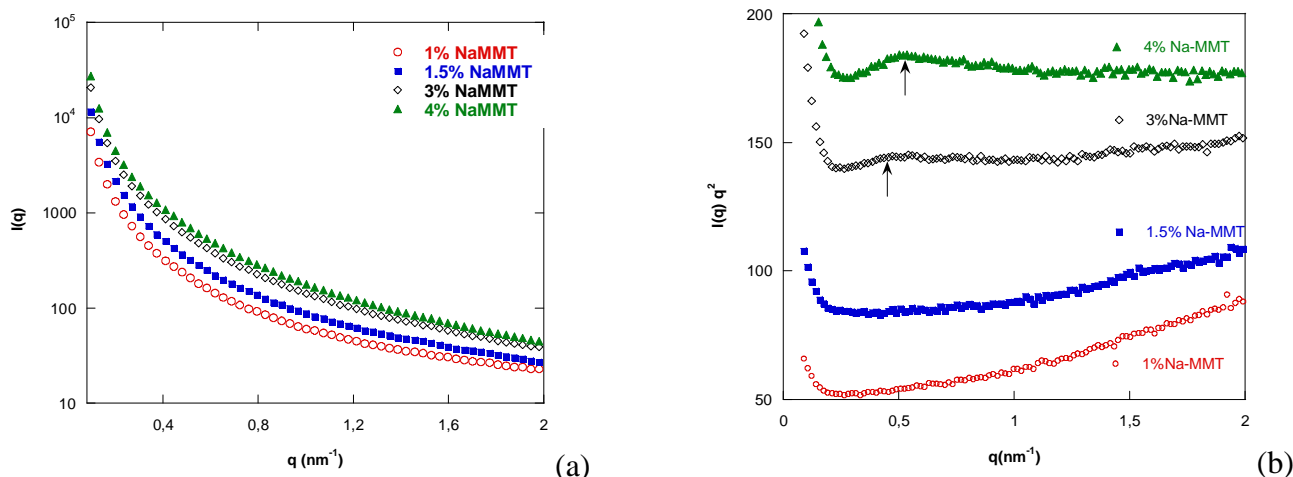
Figure 3. (a) Plots of I(q) vs q, and (b) Porod plots for Na-MMT aqueous dispersions with different clay contents.

Porod plot analysis (I(q)·q^2 vs. q plot) of the obtained scattering intensity data was performed for these Na-MMT aqueous dispersions are presented in Figure 3b. As it can be observed, no peak appeared for the 1 and 1.5% Na-MMT dispersions in water, while the 3% and 4% dispersions presented a broad peak. The presence of the peak was attributed to the platelet-platelet interaction. The position of the peak for the 3% Na-MMT dispersion was 0.45 nm^{-1}, corresponding to a distance of 14 nm (calculated using the equation: $d = 2\pi/q$), while the position shifted to higher q for the 4% Na-MMT dispersion, to 0.53 nm^{-1}, which corresponded to a distance of 12 nm.

Therefore, small angle X-ray scattering of Na-montmorillonite aqueous dispersions showed that at concentrations bellow 1.5 wt%, clay platelets were fully dispersed with an average distance between platelets higher than 16nm. At higher concentrations (3 wt%) platelet-platelet interaction was not negligible and SAXS measurements detected ordered stack structures composed of two-three platelets with an average distance of around 14-16nm.
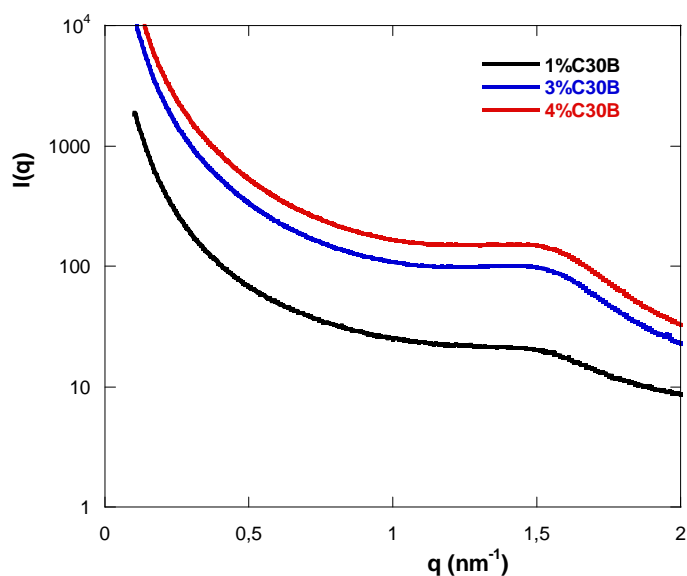

Figure 4. SAXS measurements for Cloisite 30B monomer dispersions with different clay contents.

Figure 4 shows the SAXS patterns for Cloisite 30B monomer dispersions with different clays contents. It can be noticed that the scattering intensity increased as the Cloisite 30B clay content increased, and a peak appeared at $q=1.55nm^{-1}$ which corresponds to an basal interlayer space of 4.05nm. The Cloisite 30B powder clay is characterized by a basal interlayer space of 1.85nm. Hence, Cloisite 30B clay swells in presence of the monomer mixture and the basal interlayer space increased from 1.85nm to 4.05nm.

iii) SAXS measurements of polymer nanocomposite latexes.

SAXS measurements of the liquid latexes where performed. Both the blank miniemulsion latex (S0) and the nanocomposite latexes containing different amounts of clay (S2, S3 and S4) were analysed (Figure 5). The spectrum of S0 shows the presence of the typical fringes arising from quite monodisperse spherical particles. However these fringes appeared attenuated in the spectra of S2, S3 and S4 latexes, which was attributed to the presence of clay platelets on their surface, producing a scattering typical of disk-like or rod-like particles.
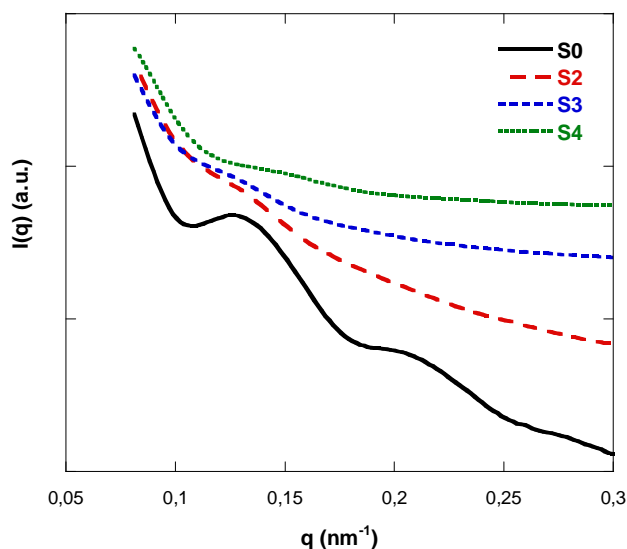
Figure 5. SAXS patterns of S0 blank latex and S2, S3 and S4 nanocomposite latexes.

Monitoring scattering intensity in time of an in-situ polymerization reaction, the evolution of the clay platelets distance during the polymerization could be pursued and could give more information about how the presence of clay platelets affect the polymer particle formation. Thus, two polymerization reactions (emulsion and miniemulsion polymerization with clay) were performed using the installations of the Chemistry lab, ID10B and IB16 beam labs of the ESRF centre. During the polymerization, samples were taken periodically (each 5 and 10 min) and monitored by SAXS. Figure 6 presents the scattering intensity profiles for different samples that were taken out during the miniemulsion polymerization reaction.
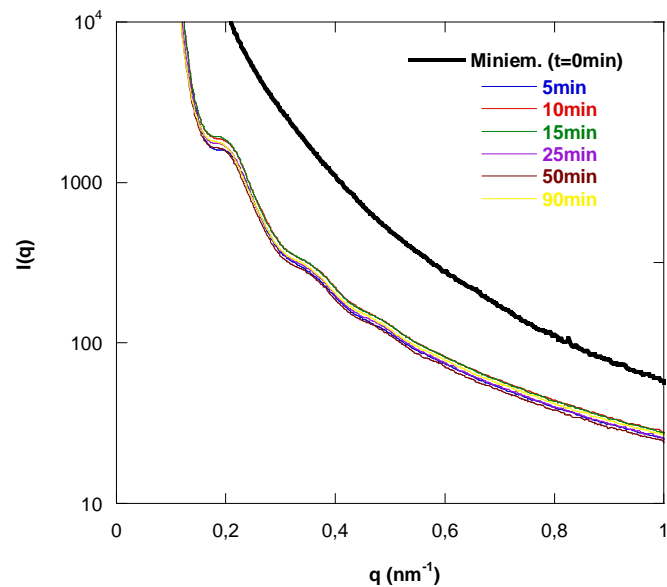
Figure 6. I(q) vs. q plots of the in situ miniemulsion polymerization at different times of reaction.
Time zero of reaction was considered the monomer miniemulsion when no initiator was added. The SAXS profile of the miniemulsion (the black curve from Figure 6) shows no peak, indicating that the ordered structure of the Cloisite 30B clays swelled in monomer (black curve from Figure 5) was lost by miniemulsification. However, once the polymerization reaction was started, no changes in SAXS profiles for the samples taken out during the polymerization were observed.

No conclusive conclusions were drawn from this series of experiments. Interesting will be to repeat these experiments inside of the experimental hutch of the beam line and to monitor on-line the evolution of the polymerization reaction by SAXS.