

**Experiment title:**

SAXS measurement of waterborne polymer/clay nanocomposites.

Experiment number:

16-02-4

Beamline:

BM16

Date of experiment:

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Date of report:

21/07/06

Shifts:

6

Local contact(s):

Dr. Francois FAUTH

*Received at ESRF:***Names and affiliations of applicants (* indicates experimentalists):****Ms. Gabriela Diaconu*, Dr. Joserra Leiza* and Dr. Maria Paulis***

Grupo de Ingeniería Química

Facultad de Químicas

Universidad del País Vasco / Euskal Herriko Unibertsitatea

Avda. Manuel de Lardizabal, 3

20018 Donostia-San Sebastián

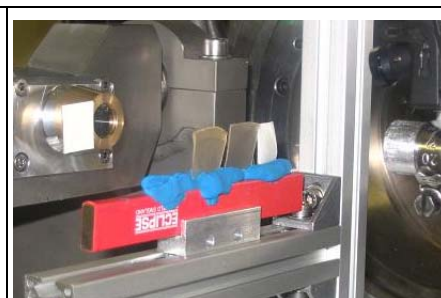
Spain

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. Small angle X-ray scattering, SAXS, presents several advantages over other exfoliation detection techniques as TEM (not an average interlayer space obtained) or WAXD (only available from 2° on: below 3nm of interlayer space).

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. The monochromatic X-ray beam wavelength was $\lambda=0.1\text{nm}$. 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.

Three sample types were measured: Clay powders and liquid latex samples were measured inside a nut covered with adhesive Kapton film (see Figure 1), and nanocomposite polymer films were measured as prepared (see Figure 2).

*Figure 1. Clay and latex samples.**Figure 2. Polymer film samples.*

Two different series of samples were measured, one prepared by emulsion and the second one by miniemulsion.

Samples prepared by emulsion polymerization

Both liquid latex samples and solid nanocomposite polymer (PMMA-co-PBA/clay) films were measured in this case. The first surprising thing observed was a big scattering peak around $q=1.65 \text{ nm}^{-1}$ ($d=2*\pi/q=3.8 \text{ nm}$) in all the films tested, even if the film did not contain clay. The first suspect was that the emulsifier used, SLS (sodium lauryl sulphate), could be the responsible for that peak. Therefore we tried to rinse the films with distilled water overnight, to get rid of the emulsifier. As it can be observed in Figure 3, the peak disappeared after the washing, so we could assign that peak to the presence of SLS emulsifier.

Figure 4 presents the SAXS measurements of the different polymer/clay samples prepared by in situ emulsion polymerization, together with a blank where no clay was added (sample E1) and a sample prepared by physical mixture of sample E1 and Cloisite Na (sample E2). The non-rinsed samples are presented.

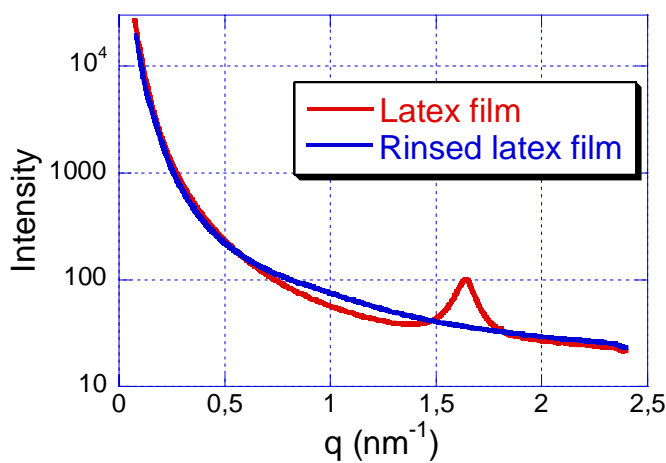


Figure 3. SAXS of latex films as prepared and after rinsing with water.

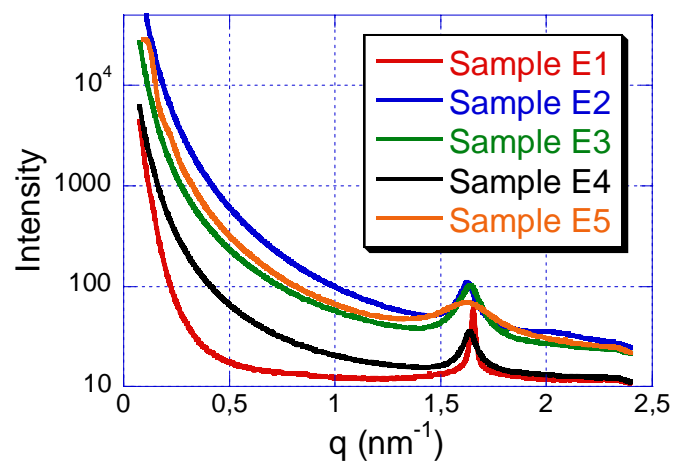


Figure 4. SAXS of latex films prepared by emulsion polymerization as prepared, prior rinsing with water.

As it can be observed in Figure 4, no extra peak apart from the SLS one appears in the SAXS patterns of the samples prepared by in situ emulsion polymerization with clay, indicating that there is not a prevailing clay interlayer distance in these spacings (between 3 and 70 nm). This could be a signal of exfoliation, if no peak appears either in the WAXD pattern (from 3nm down). It is interesting to notice the small shoulder that appears at $q=0.2 \text{ nm}^{-1}$ ($d=31 \text{ nm}$). This peak has been attributed to the core shell structure of this latex, were the peak would correspond to the presence of hard PMMA cores in the bulk of soft PBA.

SAXS measurements of the liquid latexes prepared by emulsion polymerization can be seen in Figure 5. In this case all the samples, the one prepared without clay (sample E1), the physical mixture (sample E2) and the nanocomposite prepared by emulsion polymerization with clay (sample E4) present only a shoulder at 0.16 nm^{-1} (39 nm). Therefore it can be said that the peak corresponds to the latex structure, to the latex particles mainly, and not to the clay present in samples E2 and E4.

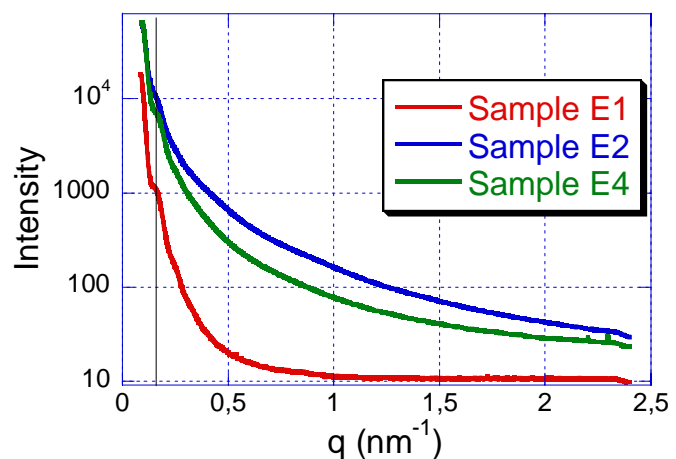


Figure 5. SAXS of liquid latexes prepared by emulsion polymerization.

Samples prepared by miniemulsion polymerization

Polymer(PMMA-co-PBA)/clay nanocomposites were prepared using both Cloisite 15A (samples M1 and M2) and Cloisite 30B (sample M3). SAXS patterns of the solid films of these samples are shown in Figure 6.

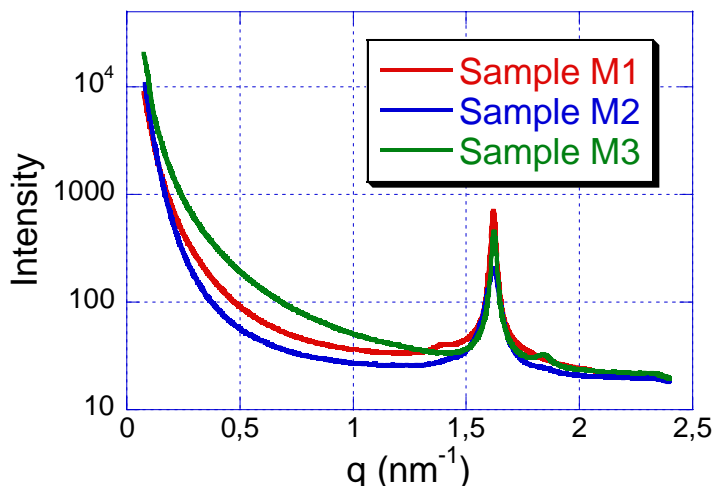


Figure 6. SAXS of latex films prepared by miniemulsion polymerization.

The peaks corresponding to the clay and the ones from the SLS were not so easy to differentiate in the WAXD patterns.

Therefore the SAXS has enabled us to see intercalation of the clay in the case of miniemulsion polymerization and a possible exfoliation of the clay in the case of latex nanocomposites prepared by emulsion polymerization.

Apart from the SLS peak present in all the samples, smaller peaks appear in the three samples, corresponding to the clay interlayer distance. In the case of sample M1, a peak appears at $q=1.4\text{nm}^{-1}$, corresponding to a clay interlayer distance of 4.5 nm. On the other hand a peak appears at $q=1.8\text{nm}^{-1}$, corresponding to a clay interlayer distance of 3.5 nm in sample M2. The initial interlayer distance of Cloisite 15A (the clay used in these nanocomposites) was 3.15nm, therefore it can be said that there has been at least intercalation of the polymer in the clay interlayer space in both samples. In the case of sample M3, prepared with Cloisite 30B, a peak appears at $q=1.8\text{nm}^{-1}$ (3.5nm). As the initial interlayer space of Cloisite 30B was 1.7nm, intercalation has also occurred in sample M3.