Shear-induced structuration of nanocomposites

based on polymers

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Nanocomposites are emerging materials that promise improved properties. However, their applicability is presently limited by the cost of manufacture and product reproducibility. These technical barriers encountered when producing high performance polymer nanocomposites on the industrial scale are due to a lack of understanding of some fundamental questions related to polymer nanocomposite technology, despite recent progress in this field. The proposed work at DESY at DORIS III on beamline BW1 equipped with a rheometer coupled to a synchrotron line [1] aims at better understanding the nanocomposite microstructure under shear and during relaxation. First experiments conducted on compatibilized polypropylene/organoclay nanocomposites are reported here.

Three different types of experiments were performed:

Effect of initial nanoclay platelet orientation relatively to the X-ray beam direction on the X-ray scattering signal:

If the clay platelets are oriented perpendicular to the beam direction (case of sheared samples or of solid samples obtained by compression molding), no X-ray scattering is detected. On the contrary, clay platelets oriented parallel to the X-ray beam direction (solid samples tilted with a 90° angle) show a typical X-ray scattering pattern of the clay (figure 1.a), with Bragg spots characteristics of the interlamellar distance between platelets and of the orientation of clay. However, having the X-ray beam parallel to the shear plane is not compatible with the use of the rheometer.

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Trials were performed in order to evaluate if a scattering pattern could be detected by shining the X-ray beam at a different angle (Laue law). Angles between 45 and 75° were investigated. Figure 1.b shows an example of SAXS pattern for a sample tilted at 75°.

These first tests showed that having an X-ray beam direction tilted with a certain angle relatively to the shear plane should allow us to probe the nanocomposite microstructure by X-ray scattering during shear and after cessation of shear.

Effect of melting and compression of the sample on the X-ray scattering signal:

The effect of melting and compression on the platelet orientation was investigated by setting a solid sample in the rheometer (platelets oriented at 90° relatively to the X-ray beam) and recording the evolution of the scattering pattern during the melting and compression steps. The evolution of the SAXS pattern is shown in figure 2.
This shows that the melting of the sample allows a disorientation of clay tactoids and that the compression step results in the immediate disappearance of the SAXS pattern due to the sudden orientation of clay tactoids by the polymer flow.

**Nanocomposite structuration after cessation of shear:**

We recently showed that the nanocomposite microstructure is not stable. The microstructure continuously changes with time due to the disorientation of the clay platelets and the build-up of a 3D filler network [2]. The nanocomposite structuration can be probed by oscillatory rheometry (successive frequency sweeps within the linear viscoelastic domain) showing a continuous increase of low frequency storage modulus plateau with time. Our purpose was to probe the platelet disorientation timescale via the appearance of a X-ray scattering pattern relatively to the timescale of the network formation via successive frequency sweeps using the rheometer-SAXS device.

However probing the formation of the filler network was impossible since the frequency sweep tests (although asked in the linear regime) were perturbed by the fact that the strain imposed by the rheometer sometimes exceeded the linear viscoelastic domain. This issue was not detected prior to our trials. The Mars II rheometer is designed to work in the controlled stress mode (mode which was checked to work properly) but also in the controlled strain mode. Our experiments were the first ones using this mode. The modification of the rheometer in order to be able to work in the controlled strain mode was already planned at the end of our experiments.

**Conclusion :**

This first set of experiments showed that X-ray scattering measurements on nanocomposites based on organoclays are possible in-situ during shear if the X-ray beam is tilted with a certain angle relatively to the shear direction. This modification of the transparent shear cell in order to have an X-ray beam direction tilted to a certain angle relatively to the shear plane is already planned for the new rheometer to be fixed on PETRA III synchrotron line during 2011. A future proposal will be made when this will be fixed in order to probe the nanoclay structuration using this unique device coupling a rheometer and X-ray scattering.

**References**
