ESRF	**Experiment title:** Organic-Inorganic hybrid networks synthesis by reactive extrusion (D2AM SAXS)	**Experiment number**: 02 01 121
Beamline: BM2 D2AM	**Date of experiment**: from: 17 June 2002 to: 22 June 2002	**Date of report**: 17 december 2002
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Report:

We studied the small angle X-ray synchrotron scattering of hybrid Silica/EVA inorganic/organic materials as a function of synthesis history and *in situ* during tensile test experiments, in order to relate their morphology to their mechanical behavior. The elaboration of these materials is new, and involve *in the molten polymer* [ref 1]:

(i) a cross-linking step of Ethyl Vinyl Acetate (EVA) polymer by Tetra PropOxy Silane (TPOS) with appropriate catalyst.

(ii) an hydrolysis step with formation of Si-OH and then condensation leading to Si-O-Si bonds.

The chemical parameters under study were:

- Cross-linking density, as deduced from swelling measurements (volume swelling ratio G_v)
- TPOS content, described by the molar ratio AV/OR of Vinyl acetate Groups (AV) divided by the number of OR groups present in TPOS .
- The hydrolysis reaction parameter OH/OR defined as the ratio of propanol (OH) groups formed by TPOS hydrolysis to remaining alkoxide (OR) groups,
- Temperature of hydrolysis (*i.e.* below and above the melting temperature of the crystallites of semi-crystalline EVA), and more generally the thermal hydrolysis history (combination of hydrolysis steps at different temperatures)
- pH of hydrolysis

A systematic study of the effect of synthesis conditions on the morphology of the obtained materials could provide evidence of a clear scenario of the morphological evens occurring during the crosslinking and hydrolysis/condensation reactions:

- Crosslinking is the key to nanostructure and yields to the formation of nanoscaled domains rich in TPOS around the chemical crosslinks.
- Hydrolysis and condensation in the nanodomains then leads to hybrid materials with the coexistence of a silica-like phase covalently bonded to the polymer.

- In the late steps of hydrolysis/condensation, particle aggregation occurs if the crystallinity of the polymer is not present (*i.e.* above the melting temperature) (figure 1). The crystallites thus act as additional physical crosslinks and strongly suppress aggregation.
- The effect of pH is shown to be similar to conventional sol-gel routes, with finer nanostructures in acid conditions, and much larger silica-rich morphology in basic pH conditions.

The mechanical properties of hybrid systems are also investigated at different levels of the synthesis. The optimum mechanical performance of the hybrid materials is always observed after the morphological aggregation step. This is concomitant with the development of reversible SAXS anisotropy with strain (figure 2), and the decrease of mechanical hysteresis of stress-strain curves (decrease of the so-called Mullins effect).

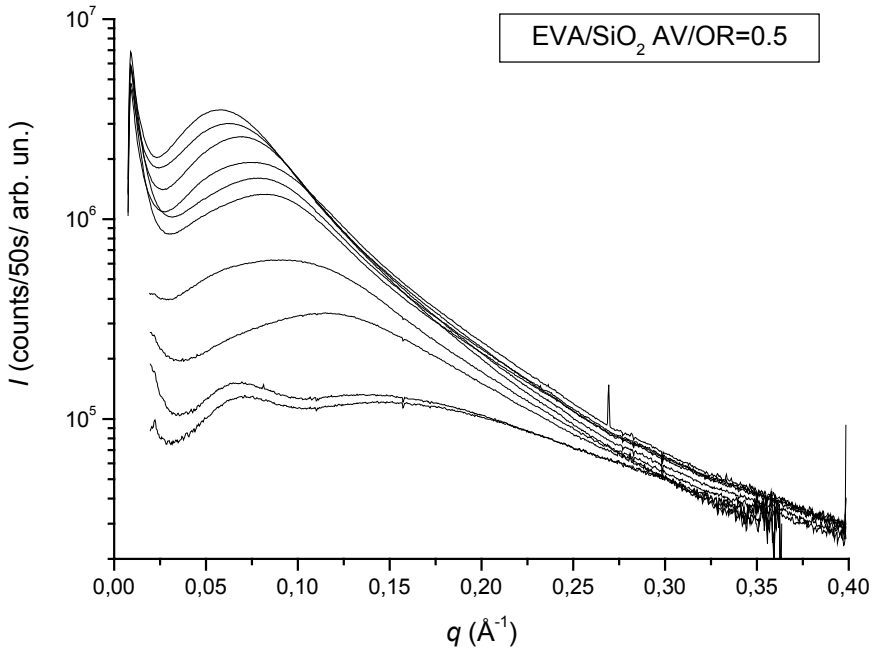

Figure 1. Evolution of scattered intensity (at T=80°C>T_f) as a function of hydrolysis time for hybrid systems with AV/OR=0.5. (0min lowest curve, 10min, 8h 18h 24h, 30h, 41h, 48h, 72h ,96h highest curve) The 'footprint' of the polymer crystallites (uncrosslinked molten TPOS-poor polymer) is present at low hydrolysis stages, and manifest as an additional correlation ring.

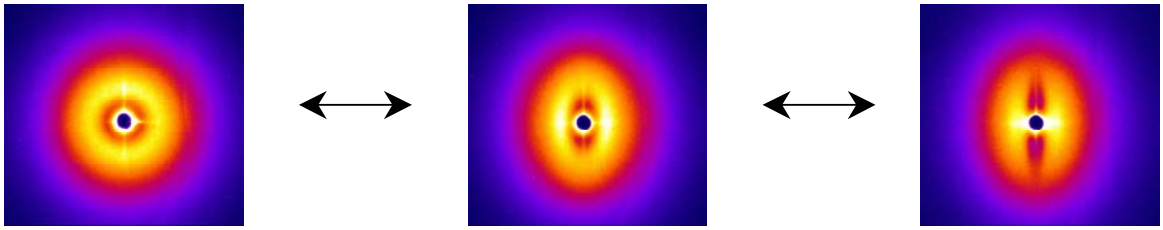

Figure 2. Evolution of scattered intensity of an EVA/Silica hybrid at ambient temperature with strain (horizontal axis). The developement of morphological anisotropy is reversible at all stages of the stress-strain curve. (AV/OR=1 hydrolysis at 80°C during 72h)

Ref 1 : Bounor-Legaré V , Ferreira I , Verbois A , Cassagnau Ph and Michel A. Polymer 2002; 43(23): 6085-6092