Standard Experimental Report

Proposal title: Carbon black percolation mechanisms probed in situ by electrical conductivity and X-ray diffraction in EPDM nano composites during cyclic loading
Proposal number: 20201662
Beamline: D2AM
Shifts: 9
Date(s) of experiment: from: 21/07/21 to: 24/07/21
Date of report: 11/02/22

- Objective & expected results (less than 10 lines): **-**

In the proposed experiment, simultaneous electrical/mechanical/structural investagations have been carried out to establish the structural parameters connected with percolation state and conductivity. The main objectives are :

- The determination of the effect of stress/strain on the microstructure of the polymer matrix (orientation, crystallization, reversibility).
- The quantitative evolution of the percolation of the carbon black aggregates during mechanical deformation.
- Relate the conductivity with scattering and deformation, as a probe of CB percolation, *in situ* during tensile testing.

- Results and the conclusions of the study (main part): **-**

Fig. 1 displays the apparent Herman's factor which quantify the molecular orientation, f_H (q = 1.36 Å^{-1}) evolution with elongation ratio for the different composite systems. The molecular orientation of polymer chains in the stretching direction is impacted by the EPDM matrix type (E1 is low diene content and E2 high diene content). Apparently, increasing the diene content decrease the orientation effects (Fig 1). Due to the rigidity (non-deformability) of the filler, some orientation could result from the localization of deformation occurring only in the polymer phase. In fact, CB nanocomposite may not be regarded as a two-phase material with individual deformations since there are high interactions at nanoscale between filler and matrix. Moreover, such systems may exhibit complex deformation processes at different length scales, such as (i) inter-aggregate reorganizations in the zones containing fewer polymer chains, (ii) simultaneous relaxation of chains occurring after large scale reorganizations of aggregates, after un-grafting of the chains from the surface of the particles or chain breakage.

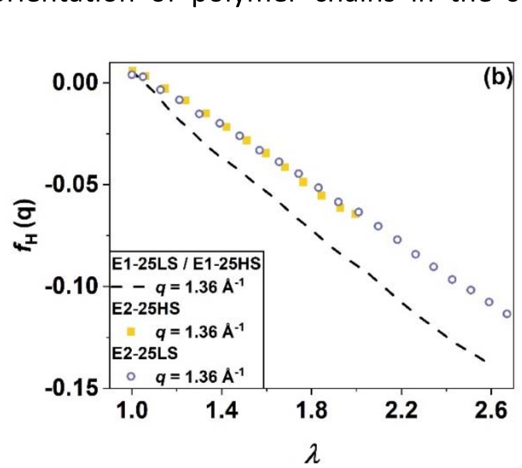

Fig. 1. The apparent Herman's factor f_H was calculated for WAXS in situ during tensile testing at q=1.36 Å^{-1} for the comparison of EPDM orientation for composites with matrix 1 or matrix 2 and as a function of CB structure during stretching.

Then the CB structural reorganization can be studied by the variation of the scattered intensities and the exponents of the generalized Porod's laws in different regions of the scattering diagrams during stretching. Indeed, such exponents are known to reflect the compaction state of aggregates. In the literature, it was reported that the morphology of CB aggregates can be studied by SAXS in the low-*q* region (q < 0.085 Å^{-1}) [1,2]. Similarly, in our data, the exponent value *a* during stretching is decreasing in the meridional direction which implies that the degree of interpenetration decreases along the stretching direction. In Fig. 2a,b, the scattering diagrams in the meridional direction ($I_{//}$) and in the equatorial direction ($I_{\perp}$) during tensile test reveal the subtle changes in CB interpenetration.

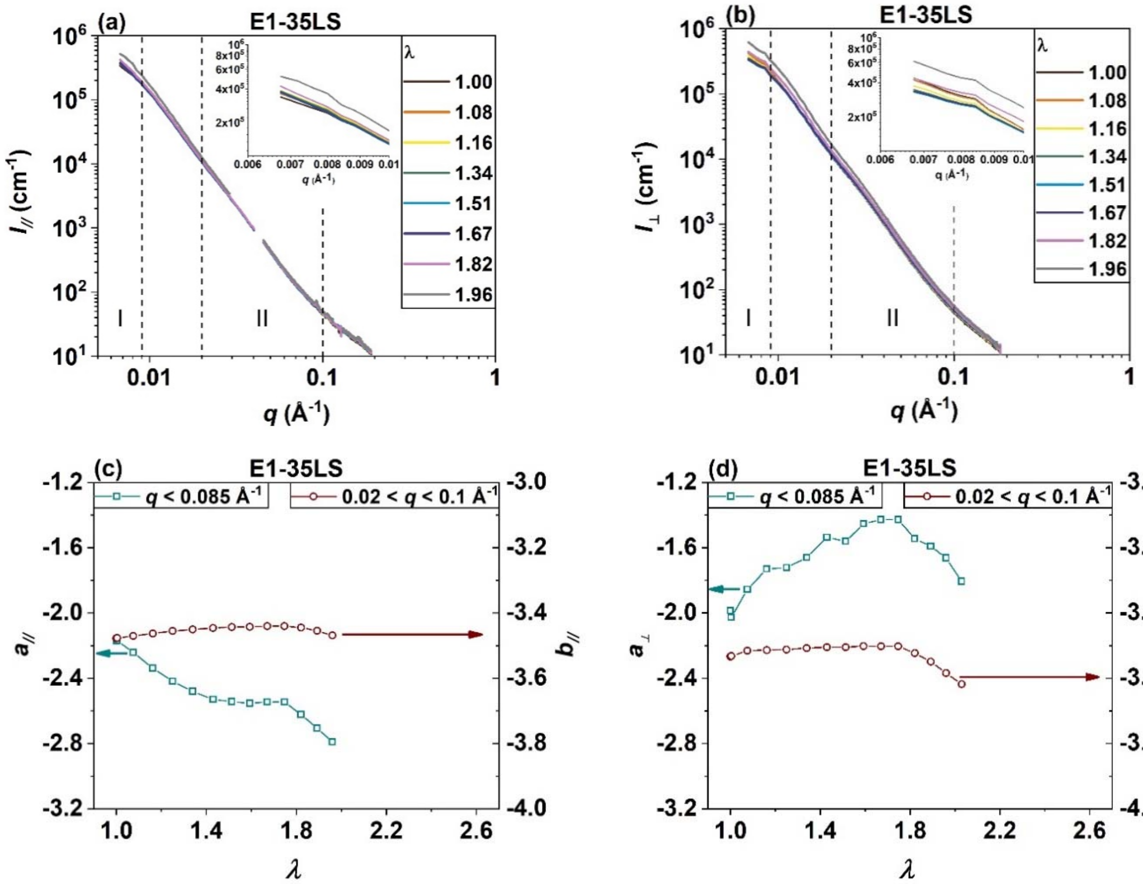

Fig. 2. (a) SAXS scattering diagrams obtained in the meridional region (*φ*=0° and 180°) (b) SAXS scattering diagrams obtained in the equatorial region (*φ*=90° and 270°) for E1-35LS during tensile test. (c) Data analyses are performed with a first generalized Porod's law $I(q)=A/q^{a}$ in the low *q* range (I) and a second power law $I(q)=B/q^{b}$ in the *q*-range II. (c) Exponents $a_{//}$ and $b_{//}$ are determined in the direction parallel to the traction (d) Exponents $a_{\perp}$ and $b_{\perp}$ are determined in the direction normal to the traction.

Fig. 2c,d displays the changes, observed in the low-*q* range (region I), in exponent $a_{//}$ (in $I_{//}$) and $a_{\perp}$ (in $I_{\perp}$) during stretching of E1 filled with 35% of low structure CB sample. The value of $a_{//}$ is decreasing during stretching, associated with a disentanglement along the meridional direction. On the contrary, the value of $a_{\perp}$ is increasing during stretching until $\lambda = 1.8$, which means that CB aggregates interpenetrate each other in the equatorial direction during stretching. This microstructural scenario is in good agreement previous to interpretations of the evolution of conductivity during stretching [3] performed on the same materials. However, at higher elongation ($\lambda > 1.8$), the value of $a_{\perp}$ is decreasing, thus revealing a different deformation mechanism. In the high-*q* region (0.02 < q < 0.1 Å^{-1}), the scattered intensity is the signature of the surface fractal of the primary CB particles, and it also follows a power law ($I(q)$

$\propto q^b$). The value of the exponent b is also reported in Fig. 2c,d, in the meridional ($b_{//}$) and equatorial ($b_{\perp}$) directions. According to the literature, the typical value for b is between -3.3 and -3.8 [1,2]. In both directions, b stays almost constant for $\lambda < 1.8$, and it is slightly decreasing for $\lambda > 1.8$. This observation is not expected to originate from a modification of the surface of primary particles (CB) since it is not affected by stretching the nanocomposite material. Therefore, this variation of b could be explained by the contribution of new scatterers such as nano-voids (nv) with net interface, thus exhibiting a more conventional Porod's behaviour with b_{nv}=-4. In order to identify if cavitation is active at large extension ratios, we evaluated the invariant (see below). As it can be found in WAXS and SAXS investigation, the equatorial region is strongly impacted by the evolution of the microstructure of CB network which occurs during stretching.

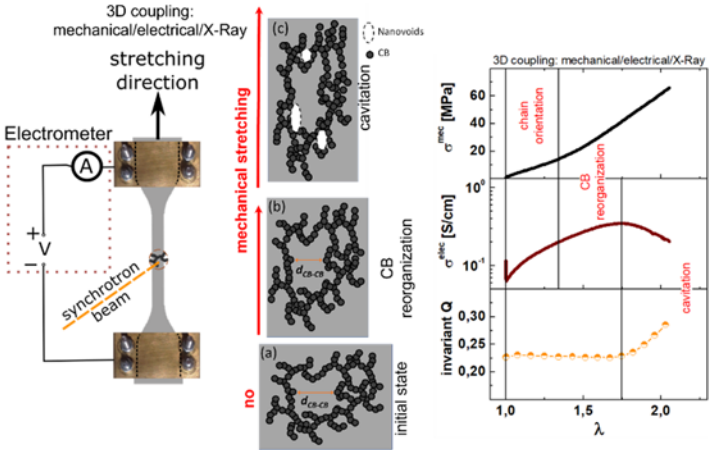

Fig. 3. Scheme of microstructural mechanisms observed with Electrical/Mechanical/Structural coupling. The increase of stress is related to EPDM orientation, the increase of conductivity is correlated with CB lateral interpenetration and decrease of conductivity is due to cavitation during tensile test

To sum up, electrical properties were correlated with tensile tests and in situ synchrotron SAXS/WAXS. Such coupling of several techniques offers a microstructural view with anisotropic reorganization of CB aggregates and nanocavitation, providing explanations of the electrical and mechanical law of behaviours. Fig. 3 synthesize the mechanisms we have identified thanks to our coupling set-up. The final decrease of the conductivity before rupture could be used as a criterion for monitoring damages that might occur in service, notably since it appears to be the signature of the apparition of cavitation.

<u>**- Justification and comments about the use of beam time** (5 lines max.): -</u>

The conductivity measurements performed under uniaxial traction on carbon black filled elastomers have revealed unexpected percolation schemes. To resolve the structural phenomena explaining these results, in situ coupled measurements of conductivity and SAXS-WAXS under traction have been performed during loading-unloading cycles (impossible on benchtop SAXS-WAXS apparatus). The results will be included in a publication.

<u>**- Publication(s)**: -</u>

[1] T.P. Rieker., et al. in Langmuir. 16 (2000) 5588–5592.
[2] F. Ehrburger-Dolle., et al. in MRS Online Proceedings Library (OPL). 661 (2000).
[3] C. Beutier., et al. in Composites Science and Technology. (2021) 109144.