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# Small angle X-ray scattering in carbon black filled elastomers : anisotropy induced at large macroscopic deformation

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**Introduction**

Reinforced rubbers used for practical applications (dampers, tyres, etc) are most often reinforced with quite highly structured (fractal) carbon black aggregates at relatively high volume fractions (up to 35%). In those regimes, filler particles strongly interact and the microscopic origin of the mechanical properties is quite different.

In order to elucidate the microscopic mechanisms which are at the origin of mechanical properties in such systems, we have investigated a series of samples filled with various types and volume fractions of carbon black aggregates. The microscopic deformation of the samples under large amplitude macroscopic strain has been investigated using Small Angle X Ray Scattering (SAXS).

The scattering by fractal carbon black aggregates has been extensively studied by various authors. According to the q-range, there are different regimes characterized by different power laws. Let us consider carbon black aggregates made of primary particles of radius *a*, of order 10 to 30 nm. For example, the N326 carbon black has elementary particles of diameter 28 nm.

For $0.1 \le q \le 1\ \mathrm{nm}^{-1}$, the so-called Porod regime (or surface scattering regime) gives a power law $S(q) \approx q^{-4}$, indicative of scattering by the surface of the elementary particles (hereafter in this paragraph called monomers). The exponent actually measured is lower than 4, of the order 3.4 to 3.7. This is because the surface of the primary particles is rough, with a surface fractal morphology. The lower limit $q_c \cong 0.1\ \mathrm{nm}^{-1}$ corresponds roughly to $q_c \cong 0.5\pi / a$ (for a polydispersity s of the order 0.30, as it is generally observed) (Hasmy 1994). The nearest-neighbor monomer distance actually coincides with the monomer diameter 2*a*. Monomer-monomer correlations are not measured in the regime q > qc, and the scattering is proportional to N, the total number of monomers within the scattering volume.

For $q < q_c \cong 0.1\ \mathrm{nm}^{-1}$, one enters the mass fractal aggregate regime, described by the power law $S(q) \approx q^{-D_m}$, where $D_m$ is the fractal dimension of the aggregates. The fractal dimension which is measured is compatible with the diffusion-limited aggregation value $D_m = 1.78$.

For separated, non correlated aggregates, this regime ends up with a Guinier regime at a scattering vector $q \cong {R_g}^{-1}$, where $R_g$ is the dimension (radius of gyration) of an aggregate.

For even smaller $q$ values ($q << {R_g}^{-1}$), another Porod regime with $S(q) \approx q^{-4}$ appears, related to the scattering by the surfaces of agglomerates of clusters (or by the macroscopic surfaces of the scattering volume itself).

The considerations above apply for separated, non interacting clusters. The limiting case corresponds to close-packed, but non-interpenetrating clusters. However, in concentrated samples, aggregates either strongly overlap, or are destroyed, at some length scale $\xi$. The mass fractal regime is not observed at $q$ values smaller than $\xi^{-1}$.

The overlapping distance $\xi$ may be estimated as follows (Sorensen 1998). Primary particles ("monomers") have a radius *a*. Let us suppose that the fractal structure (fractal exponent $D = 1.78$) is preserved up to a distance $\xi$, so that fractal sub-clusters of radius $\xi$ are close-packed. The volume fraction is then that within a fractal sub-cluster, that is $\Phi = N_\xi (a/\xi)^3$, where $N_\xi$ is the number of monomers within each element, given by $N_\xi = 1.3(R_\xi / a)^D$. $R_\xi$ is the gyration radius of the sub-cluster, related to the radius $\xi$ by $\xi = [(D+2)D]^{1/2} R_\xi$, that is $\xi \cong 1.45 R_\xi$, which finally gives $\Phi = 0.67(\xi / a)^{D-3}$. For $\Phi = 0.33$ (corresponding to a weight volume fraction 0.5) for example, this gives $\xi \cong 2a$.

This rough estimate obviously indicates that aggregates interpenetrate very strongly, or are broken, in the quite concentrated samples studied here, at a spatial scale which is not at all large compared to the size of the primary particles.

For $q < \xi^{-1}$, the system is homogeneous and the scattering function $S(q)$ should be flat, which has indeed been already observed (Sorensen 1998). The scattering from the system comes from large scale fluctuations of the carbon black density and from the surfaces of the whole scattering volume.

It is not clear which effect contributes predominantly in this very small $q$ regime ($q$ typically ranging from a few $10^{-3}$ to a few $10^{-2}$ $nm^{-1}$). Scattering from the surfaces of the sample volume gives a Porod law $S(q) \approx q^{-4}$. It is indeed a difficult task to extract some information on large scale concentration fluctuations from this $q$ regime. This point will be discussed later in this paper.

In the experiments presented here, we combine SAXS and large amplitude mechanical stretching to study how the composites deform at spatial scales close to the interpenetration distance $\xi$. This study has been more specifically focussed on two questions, which are nevertheless closely related to each other: does the long time mechanical relaxation observed in these systems result from observable carbon black aggregates slow reorganisations; and second, can the plasticity observed in these systems be correlated to large scale reorganisation of the carbon black aggregates under large macroscopic strain, and does it correspond to an induced residual measurable anisotropy at the scale of the carbon black aggregates ? We shall see that the answer to both questions is negative, which in turn rises more questions about the processes involved in large amplitude deformations of these systems.

## Experiments

### Samples

Samples are made of synthetic poly(isoprene) sulfur vulcanized matrix. Carbon black is mixed using classical Brabender dispersion. Different types of carbon blacks were used, with various particle sizes and structures. Samples are provided by Michelin. Characteristics of the samples are summarized in Table I.

| Sample name | Type of CB | CB volume fraction | Sulfur/accelerator |
|---|---|---|---|
| 1 | N358 | 50pce | 1.5phr |
| 2 | N326 | 50pce | 1.5phr |
| 3 | N765 | 50pce | 1.5phr |
| 4 | N772 | 50pce | 1.5phr |
| 5 | N358 | 30pce | 1.0phr |
| 6 | N358 | 13.26 wt % | ? |

Samples were 0.3 to 0.5 mm thick sheets cut in an injection molded bulk sample of section 25 × 31 mm. Samples of dimensions approximately 25 × 5 mm were cut in each sheet. Samples were held in a home-made drawing apparatus which allows to uniaxially stretch the sample at a fixed draw rate $\dot{\varepsilon}$ (up to 10 mm/sec) and then let the sample relax to zero constraint. Oscillatory draw cycles of various amplitude may also be applied to measure the modulus. The relaxation of the force (constraint) may be studied as a function of time, at a constant draw ratio $\varepsilon$. The draw ratio $\varepsilon$ is defined as $(L - L_0)/L_0$.

### SAXS experiments

Scattering experiments were performed at the European Synchrotron Radiation Facility (ESRF), Grenoble, France, on the BM2 beamline. The incident beam section at the sample is of the order

$100 \times 100$ μm. The incident energy was 8 keV, which corresponds to a wave length $\lambda = 0.1552$ nm. The distance between sample and detector was 2 m, with a small gold cylinder of 1 mm diameter (fixed on a capton foil) used as a beamstop. A 2D indirect illumination CCD detector (Princeton Instruments) was used. The pixel size is 50 μm, which corresponds to a resolution $10^{-4}$ Å$^{-1}$. In these conditions, the minimum value of the scattering vector was $10^{-3}$ Å$^{-1}$ ($10^{-2}$ nm$^{-1}$). The 2D patterns were corrected to eliminate a slight bias in the detector response, as well as the dark current signals and background scattering. The signals were normalised for sample transmission.

We have selected a $q$-range which corresponds to the inverse of the expected vicinity of the interpenetration distance $\xi$. The behaviour at larger $q$ values, which corresponds to the scattering by the volume and surface of primary particules, has been already extensively studied. We thus restrict ourselves to this limited range of $q$, approximately $10^{-3} \le q \le 10^{-2}$ Å$^{-1}$ (or $10^{-2} \le q \le 10^{-1}$ nm$^{-1}$).

**Results.**

**Unstretched samples are anisotropic**

It has already been observed that the scattering from as prepared-samples is anisotropic. The same phenomenon appears here. Samples studied here are blended in the molten state using brabender dispersion and then injection-moulded. A quite significant anisotropy is indeed observed in practically all samples studied. To illustrate this, the two dimensional SAXS pattern obtained in sample 1 is shown in Figure 1. The pattern shows isointensity contours which are elliptical in the approximate range $1.5\times10^{-2} < q < 2.5\times10^{-2}$ nm$^{-1}$. The magnitude and direction of the anisotropy (the direction of the principal axis of the ellipse) depends on the considered sample.

The intensity profiles corresponding to the 2D patterns shown in Figure 1 are shown in Figure 2. The intensity profiles are shown in two directions corresponding to the principal axis of the observed elliptical 2D contour patterns. The same behaviour is observed in both directions, with an upward shift in intensity in the direction of the long axis. Two regimes are observed according to the $q$ range. There is an apparent power law with an exponent of the order $-2.1 \pm 0.1$ in the q range $0.01 \le q \le 0.08$ nm$^{-1}$, where the mass fractal regime should be observed. For $q \ge 0.08$ nm$^{-1}$ the exponent is of the order –3.5. In all samples, the crossover is very smooth. In sample 3, which has larger carbon black primary particles, the crossover is shifted towards small q values (perhaps around 0.03 to 0.04 nm$^{-1}$), so that the mass fractal regime (with apparent exponent –2.1) is hardly visible.

**2D pattern obtained in stretched samples**

An anisotropy is induced in the 2D SAXS patterns upon uniaxially stretching the samples at large amplitude. The overall pattern results from a combination of the original anisotropy in the relaxed sample (which has an arbitrary direction with respect to the draw axis), and the anisotropy induced upon stretching (which has the symmetry of the draw experiment). The changes induced in the 2D scattering patterns on increasingly stretching the samples are shown in Figures 3 to 5. These figures show the typical patterns described in (Rharbi 1999), with 4 intensity reinforcements which are well visible in Figure 5b. Figure 3c deserves special attention: it shows a significant intensity reinforcement in the perpendicular direction (perpendicular to stretching).

Apart from that in Figure 3c, 2D patterns obtained at high stretching in all three samples 1,2 and 4 are qualitatively similar. These samples differ only by the nature of the carbon black.

**Effect of the carbon black concentration**

Figure 6 shows the 2D patterns obtained in the less concentrated sample 6. The anisotropy induced in the pattern at a given draw ratio is more pronounced in this case. The intensity reinforcement is located in the perpendicular direction.

**Relaxation of the induced anisotropy**

The kinetics of relaxation of samples stretched up to high draw ratios have been observed, by combining force and 2D SAXS measurements (at fixed draw ratio), over time scales extending from a few seconds to a few tens of hours. Whereas the force relaxes significantly over this duration, absolutely no change is observed in the 2D scattering patterns obtained.

**Discussion.**

**Relaxed samples**

The different regimes observed in the intensity profiles correspond to those already observed (Ehrburger-Dolle 2001). The exponent –3.5 observed for $q \geq 0.08$ correspond to the Porod regime, i.e. the scattering by the surface of the elementary particles, which has a fractal surface structure. The range $0.01 \leq q \leq 0.08$ should correspond to the mass fractal regime. In this regime, the exponent –1.8 is observed in non interacting aggregates (fluffy carbon black), whereas a smaller apparent exponent (typically of the order –1) is observed in concentrated carbon black filled systems. This weaker scattering law indicates that the system tends to become isotropic at larger scale, due to the strong interpenetration of aggregates which smear out the fractal distribution of primary particles in space.

However, a larger exponent is observed here. The interpretation of the power law –2.2 observed in this q-range is not clear at this point.

The scattering profiles show no tendency to rise up at very small angles (close to the center), as it is expected from macroscopic surface scattering (Sorensen 1998). This indicates that this regime would appear at scattering angles even smaller than $10^{-2}$ $nm^{-1}$, and that no large scale heterogeneities (agglomerates of clusters) are detected here.

The anisotropy of the 2D patterns obtained in the relaxed samples is observed in a q range $0.01 \leq q \leq 0.03$ $nm^{-1}$ which corresponds to a spatial scale 3 to 10 times larger than the primary particles radius. Such an anisotropy has already been observed. It is due to the method of preparation of the samples by injection moulding, which implies strong constraints on both the polymer chains and carbon black aggregates. Polymer chains can reorient and relax during curing, and show no residual orientational order in the relaxed samples, as it may be evidenced by NMR experiments. However, relaxing carbon black aggregates probably requires much longer relaxation times, which compete with the reaction rate during curing.

**Stretched samples**

X,Y “double wing” and “butterfly” isointensity contours have been already observed in elongated soft-hard nanocomposites samples. These patterns have strong similarities with those observed herein. They have been interpreted in terms of a local shear process (Rharbi 1999, Oberdisse 2000). 2D numerical simulations have been performed to study how inter-aggregate correlations are affected upon deforming (stretching) the matrix.

The local shear process means that local deformation is non affine, or equivalently, that some reorganisation occurs at the spatial scale investigated upon large amplitude macroscopic deformation. This rises the question of the time scale of such reorganisations. It is observed macroscopically that the force measured macroscopically at a large, fixed draw ratio, relaxes in a strongly non exponential way on time scales ranging from seconds to tens of hours. Remarkably, no measurable change in the scattering pattern is observed during the relaxation.

Another question concerns the reversibility of the reorganisations. Filled elastomers generally exhibit plasticity. So do the samples studied here. A residual macroscopic deformation of a few percent is observed. It relaxes over very long time scales as well, and its amplitude depends on the volume fraction and nature of the carbon black filler. No plasticity, that is, no residual anisotropy, is observed in the SAXS patterns after stretching the sample to a large draw ratio and having it relax to zero stress. More precisely, no measurable difference is observed in the SAXS patterns before and after a large amplitude draw cycle. It should be noted however that 2D patterns are in fact not very

sensitive to the macroscopic anisotropy. The intensity profiles measured in directions perpendicular and parallel to the stretching directions differ only slightly when the sample is stretched up to 400%. Also, the anisotropy which is present in the 2D patterns from relaxed samples is qualitatively of the same order as that induced upon stretching. This indicates that the microscopic constraints applied during injection of the molten, blend samples and then frozen during curing are extremely large.

**Conclusion**

The points which remain to be clarified are:

1. elucidating the apparent –2.1 power law exponent in the scattering profiles in the range $0.01 \leq q \leq 0.03$ nm$^{-1}$ or $0.01 \leq q \leq 0.08$ nm$^{-1}$ (according to the size of primary particles). Indeed, this power law contradicts the fact that concentrated samples are expected to be *more* homogeneous than isolated fractal aggregates (at scales larger than the diameter of primary particles), which have a power law –1.8, and thus are expected to give a power law decreasing *less* rapidly than $q^{-1.8}$.

Specifically, the contributions from additives and from microcrazes have to be estimated and substracted.

This implies varying systematically the volume fraction of the samples, to check whether the expected –1.8 law is recovered at low volume fractions.

2. analysing the anisotropy induced in the stretched samples. This includes performing numerical simulations to estimate quantitatively the magnitude of the anisotropy reflected in the 2D SAXS patterns and compare it to the macroscopic imposed anisotropy.

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**a** **b**

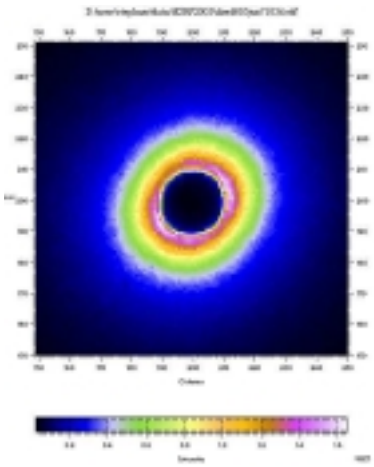

**Figure 1**

Two-dimensional SAXS patterns for **a** : sample 1 (50pce N358); **b** : sample 2 (50pce N326). The square picture is 100 × 100 pixels, which corresponds to a $q$ range $0 < q < 5\times10^{-2}$ $nm^{-1}$.

**a** **b**

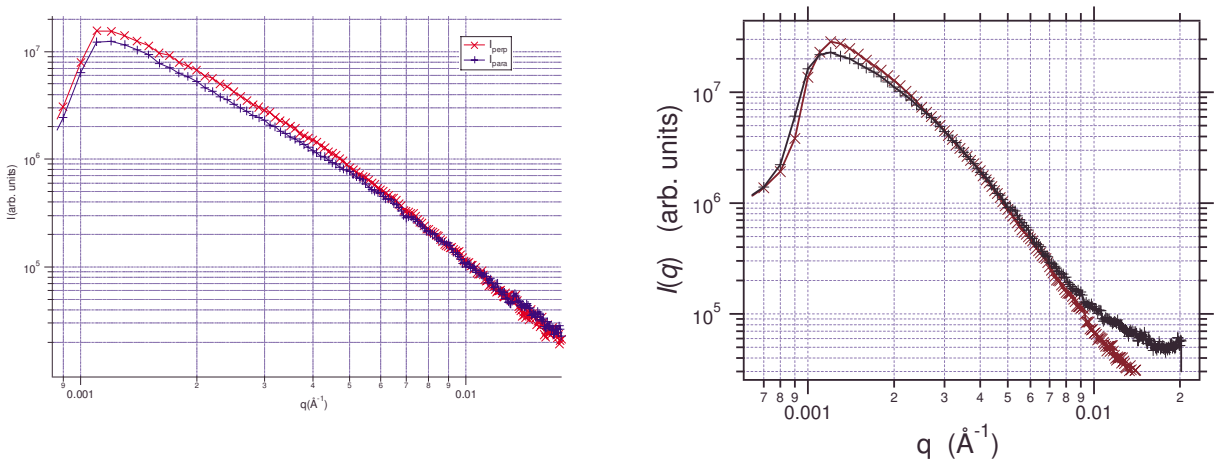


**Figure 2**

Intensity profiles corresponding to the 2D patterns shown in Figure 1: **a**: sample 1; **b**: sample 3. Note that the $q$ range here is larger than in Figure 1.

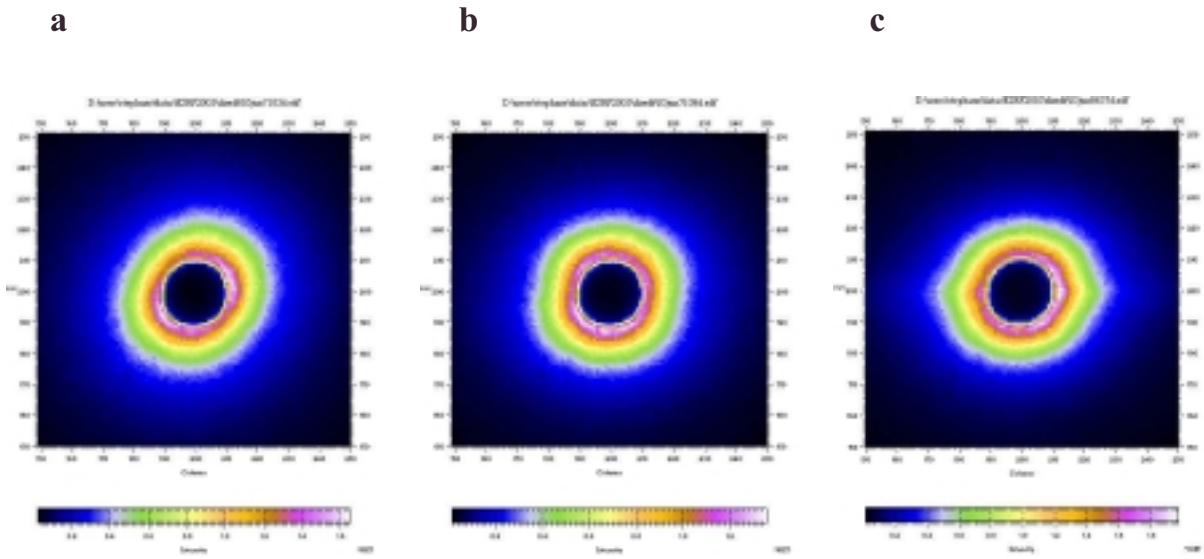


**Figure 3**

Two-dimensional SAXS patterns for sample 1 (50pce N358) at increasing draw ratios: **a** : ε = 0, **b** : ε = 300%, **c** : ε = 500%. The stretching direction is vertical. The square picture is 100 × 100 pixels, which corresponds to a $q$ range $0 < q < 5\times10^{-2}$ $nm^{-1}$.

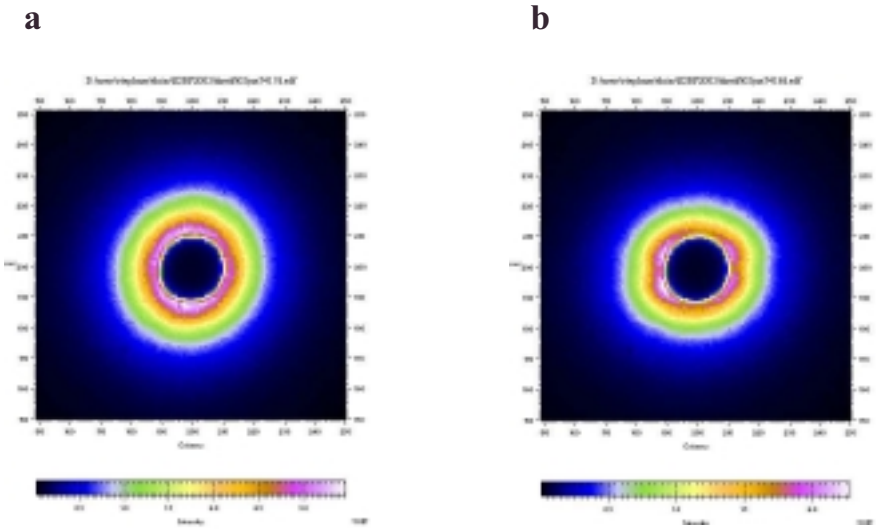


**Figure 4**

Two-dimensional SAXS patterns for sample 4 (50pce N772) at increasing draw ratios: **a** : ε = 0, **b** : ε = 300%. The stretching direction is vertical. The square picture is 100 × 100 pixels, which corresponds to a $q$ range $0 < q < 5\times10^{-2}$ $nm^{-1}$.

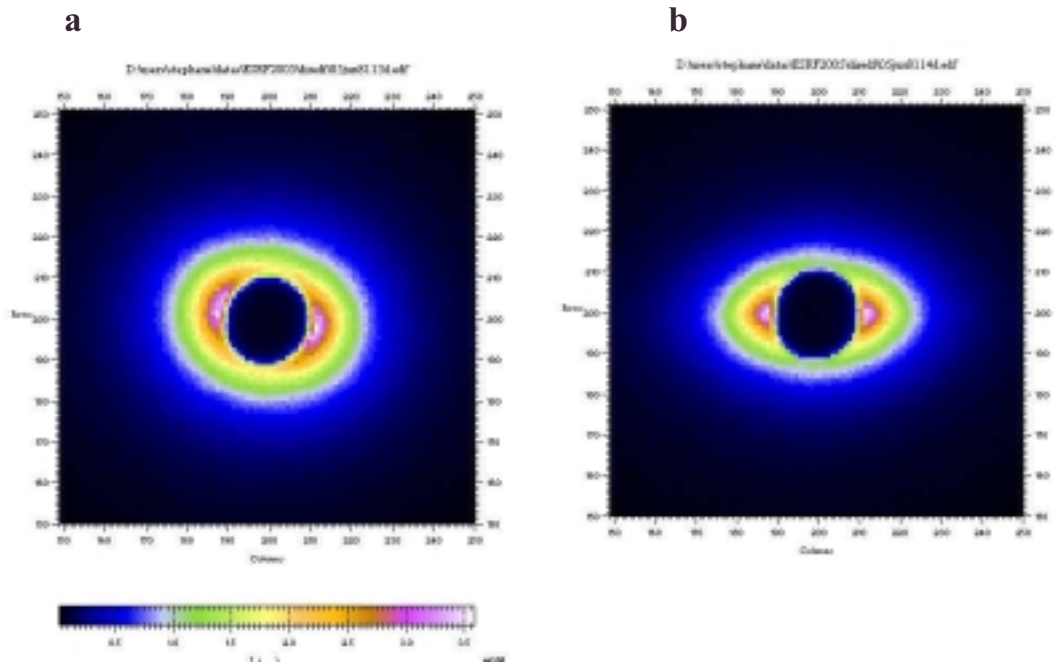


**Figure 5**

Two-dimensional SAXS patterns for sample 6 (13.26 wt% N358) at increasing draw ratios: **a** : $\varepsilon = 0$, **b** : $\varepsilon = 400\%$. The stretching direction is vertical. The square picture is $100 \times 100$ pixels, which corresponds to a $q$ range $0 < q < 5 \times 10^{-2}$ $nm^{-1}$.