Nanoparticles reorganizations in polymer nanocomposites under large deformation

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The structural evolution of nanoparticles (NPs) dispersion under uniaxial stretching and extension/retraction deformation cycles above $T_g$ was investigated in model silica/polymethylmethacrylate (PMMA) nanocomposites (PNCs) by a combination of Small Angle X-ray Scattering (SAXS) and Transmission Electronic Microscopy (TEM). The different structure displacements and reorganizations can be quantitatively characterized as a function of elongation ratio, silica volume fraction and NP size. At low NP volume fraction, a rotation/orientation of non-connected aggregates is observed along the stretching direction, while the reinforcement is low and might be limited by the large-scale aggregates. At high volume fraction, the stress–strain curves exhibit three regimes. (i) At low stretching ratio, in the linear deformation regime, reinforcement is driven by the primary network filler structure. (ii) Above a few percent of deformation, a yield is observed and can be associated to the network breakdown as revealed by cyclic extension/retraction experiments. (iii) As a result of this yield, at larger deformation, the stress curve appears as shifted upward with respect to the one of pure polymer. A persistence of this vertical shift (constant value up to large deformation) might be related with SAXS measurements to a non-affine deformation of the NPs network due to new structural arrangements, while in a second case, the decrease of stress to the pure polymer value with increasing deformation is related with observation of affine deformation after the yield. Finally, affinity and non-affinity after yielding are discussed for all the systems according to the strength of the NP–NP interaction.

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1. Introduction
Polymer nanocomposites (PNCs), consisting of nanoscale fillers dispersed in polymer matrix, exhibit enhanced mechanical properties compared to the unfilled matrix on a large range of deformation. The fillers contribute differently to the reinforcement according to their size, shape or volume fraction. At low volume fraction and low deformation (typically below 5%, i.e. in the linear regime), strong increases of elastic modulus and terminal time have been mainly reported [1–5]. At high volume fraction, it is now commonly admitted that the main contribution, which has to be considered to explain the large enhancement of mechanical properties is the existence of a “filler network”, i.e. when the particles are arranged in a connected structure.

However, the mechanical behavior at medium and large deformation (above 5%) leads to many unsolved questions. For instance, for filled elastomers, in the low deformation regime a decrease of the oscillatory storage modulus is commonly observed when the amplitude of the imposed oscillation is increased (the so-called Payne effect [6]), while in larger deformation regime during load-unload cycles, mechanical hysteresis is observed, with an appreciable change in mechanical properties after prestraining (the Mullins effect [7,8]). Many explanations have been proposed. Payne effect could be related to desorption of chains immobilized at the filler surface [9], to slippage of entanglements (slip-links) of higher density at the surface or to release of occluded polymer trapped in filler agglomerates, or to the existence of $T_g$ gradient around the NPs [10,11]. Other models implying structural filler rearrangements (non-affine reorganizations, cyclic filler network breakdown with rupture/re-agglomeration process) [12] have been proposed to explain the deformation dependence of the storage modulus. Beyond these different processes involving the multi-scale structure of the NPs (from the individual NP to large aggregates or
agglomerates), the question of the relevant scale of the filler reorganization remains a challenging issue.

In this context it is useful to well characterize the structural filler evolution under deformation at all relevant scales. For deformation large enough to give measurable changes (>10%), Small Angle Scattering (SAXS) measurements, using X Rays (SAXS) or neutron (SANS) radiation, are the most suitable techniques to investigate the deformation-induced phenomena at the submicron scales in many polymer systems such as polymer networks [13–17], gels [18], elastomers [19] or fibers [20], and phase transition in crystalline polymer [21]. SAS is also convenient for studying various nanocomposites [22–31].

In such SAS measurements on stretched polymer systems, the anisotropy is observed through the 2D patterns of the scattering from either labeled chains (using SANS), or filler embedded in the deformed matrix (SAXS or SANS). These patterns display different shapes: ellipse, eight shaped butterflies or double wings. In the two latter cases, mostly observed for NPs scattering, two or four maxima can be present depending on the strength of the correlations. The scattering intensity depends on both the form factor of the concerned objects and the structure factor coming from their interactions. When deformation affects the objects (chains, deformable aggregates) as much as it affects the inter-objects distances, the observed patterns are elliptical. When the scattering objects are less deformed (more cross-linked regions, hard NPs) than the matrix, and therefore than the inter-objects distances, a butterfly (or double wings) pattern is observed. In nanocomposites, this particular pattern has been observed earlier by SANS by Rharbi et al. [22]. They reported affine displacement of particles centers at low deformation while, for higher stretching, 4 spots pattern is observed and interpreted as local stress inducing particle avoidance. These experimental observations have been supported by further simulations [32]. Non-affine deformation has also been reported in others systems characterized by their heterogeneous spatial distribution of modulus like in large and small chains mixtures, cross-linked polymers [13–16], gels [18,33], latex films [34,35], filled elastomers [23] and copolymers systems.

The investigation of filler deformation in PNCs has also been reported using Transmission Electronic Microscopy (TEM) [36,37] or Atomic Force Microscopy (AFM) [38]. These techniques give pictures in the real space thanks to good contrast between particles and polymer. Le Diagon et al. [38] evidenced the loss of affinity at the inter-particles scales by AFM, while at larger scale the deformation remained affine. Yatsuyanagi et al. [39] revealed by TEM the breakdown of the filler network that could release occluded polymer and thus decrease the modulus at high deformation.

Recently we investigated the chain conformation by SANS in silica/poly(styrene) (PS) nanocomposites (PS-PNCs) highly stretched above Tg [40]. Some chains were labeled by deuteriation and the silica scattering was matched using zero-average appropriate contrast. The results showed no changes in chain conformation in deformed filled polymers compared to the deformed unfilled one, indicating that glassy state should only concern a small fraction of chains, while reinforcement remains still higher at large deformation, suggesting the influence of filler reorganizations. Here we complement this previous work by focusing now on such filler’s displacements under stretching above Tg, and on their correlations with mechanical reinforcement occurring at medium and large deformation. Silica dispersion states at rest have been previously well characterized in different systems (PS [4] and PMMA [41]) and two regimes of concentration have been observed: non-connected aggregates at low silica volume fraction and connected network for larger volume fractions. In this paper we report on the structural evolution in both dispersion regimes of silica spatial distribution under large deformation by combining SAXS and TEM to get access to the largest size range. Using complementary mechanical measurements, we propose to gain understanding about the role of silica displacements in the observed reinforcement under large deformation. For this we consider model silica/poly(methylmethacrylate) (PMMA) PNCs, for which by varying the NP nature, we can produce different behaviors. Additional data on PS PNCs will be given in SI, which lead to consistent results. Note that our systems are different from reinforced rubbers because the chains are not cross-linked, but, as detailed in the Results and Discussion Section, the characteristic time range of the deformation applied here is several orders shorter than their terminal times, so the polymer matrix is in an elastic “rubbery” regime.

2. Materials and methods

2.1. Samples preparation

Nanocomposites were prepared by mixing a suspension of silica NPs, initially dispersed in an organic solvent, the DiMethylAcetamide (DMAc, boiling point 167 °C), with a polymer solution (10%w/v). The mixture is stirred for 2 h and then poured into Teflon moulds and let cast by solvent evaporation in an oven at constant temperature (130 °C) during 8 days to ensure complete drying. At the end we obtained PNC films of dimension of 5 cm × 5 cm × 0.1 cm with less than 1%wt in residual solvent. Poly(methylmethacrylate) (PMMA) has been purchased by Sigma Aldrich with an average molecular weight, Mw, of 350 000 g/mol (Ig ~ 2). The different silica beads used have been characterized by Small-Angle X-rays scattering (SANS) [41]. One silica solution, already dispersed in DMAc (Nissan-St), was purchased from Nissan Chemical with a radius of R = 6 nm and polydispersity of σ = 0.34 and two others silica solutions (Ludox TM-40: R = 13.8 nm with σ = 0.15, and Ludox LS:...
$R = 7.4$ nm with $\sigma = 0.16$) were purchased from Sigma Aldrich as dispersions in water, and then transferred by us in DMAC. During the transfer Ludox stability is ensured: we compared SAXS curves in the two solvents before and after transfer (SAXS measurements in water are not shown here) and the curves well superimpose: we do not observe any aggregation due to the change of the solvent, so the Ludox silica are as well dispersed in DMAC as the Nissan silica. In this paper we will also compare the results for PMMA matrix with the ones for a PS matrix ($M_w = 280$ 000, $I_p = 2$) where Nissan particles have been dispersed using the same method, as described in our previous work [4], and which have been studied using the same techniques. The results for the PS are shown in SI.

2.2. Mechanical properties: uniaxial stretching experiments

For uniaxial stretching, rectangular films of 2 cm $\times$ 0.5 cm $\times$ 0.1 cm are cut and carefully sanded down to a constant thickness. Samples are stretched up at $T_g + 20$ °C (Glass-transition temperatures $T_g$s were determined by Differential Scanning Calorimetry (DSC) [41]) in an oil bath to a predefined deformation with a constant rate deformation $\frac{dx}{dt}$ of 0.005 s$^{-1}$ using a homemade apparatus ($\lambda$ is the elongation ratio defined as $\lambda = L(t)/L_0$). The tensile force is measured with a HBM Q11 force transducer and converted to real stress by dividing the force by the assumed cross section during the elongation. The good homogeneity of the stretching is followed thank to grid lines drawn on the samples (see the photograph on Fig. 1). Finally sample is quenched at room temperature below $T_g$ for further SAXS recording in the synchrotron facility. Note that the duration of quenching, around 10 s, is much shorter than the relaxation times necessary for rearrangements of particles aggregates under constant deformation at the relevant scales studied by scattering. We also performed extension/contraction cycles. The imposed length cycle is composed of i) an extension until $\lambda = 2$ with a stretching rate $\frac{dx}{dt}$ of 0.005 s$^{-1}$ followed by ii) a return to $\lambda = 1$ at the same rate. During or after this return the sample is let free to recover (or not) its initial length. Note that in all deformations processes applied here, the characteristic times are much shorter than the relaxation times. So we can consider here that the material behaves as permanently entangled, i.e. as an elastomer. This will be detailed in the section Results and Discussion.

2.3. Small-angle X-rays scattering (SAXS)

Small Angle X-rays Scattering (SAXS) experiments were performed at the ESRF on ID-02 instrument. We used the pinhole CCD camera at the energy of 12.46 keV at two sample-to-detector distances (1 m and 10 m) corresponding to a $q$-range between 0.0008 Å$^{-1}$ and 0.3 Å$^{-1}$. The absolute units are obtained by normalizing respect to water (high $q$-range) or Lupolen (low $q$-range) standard. In addition, for some samples, a Bonse-Hart camera set-up was used, allowing reaching $q$-range lower than 0.0008 Å$^{-1}$ (the lower limit is set by the strength of the sample scattering).

For stretched samples the SAXS iso-intensity contours on the 2D CCD detector are anisotropic and the corresponding intensities $I_{\|}(q)$ and $I_{\perp}(q)$ are radially averaged along a given direction within an angular sector of axis parallel ($\parallel$) or perpendicular ($\perp$) respectively to the stretching. Fig. 1 presents a schematic representation of anisotropic data analysis. For the Bonse-Hart measurements, the scattering was recorded along one direction at a time, either parallel or perpendicular to the stretching axis.

2.4. Transmission electronic microscopy (TEM)

The samples were cut at room temperature by ultramicrotomy using a Leica Ultra cut UCT microtome with a diamond knife. The cutting speed was set to 0.2 mm s$^{-1}$. The thin sections of about 40 nm thicknesses were floated on deionized water and collected on a 400-mesh copper grid. Transmission electron microscopy was performed on a FEI Tecnai F20 ST microscope (field-emission gun operated at 3.8 kV extraction voltage) operating at 200 kV. Precise scans of various regions of the sample were systematically done, starting at low magnification, which was then gradually increased. The structural information on aggregates has been extracted from their projected images using the software ImageJ (see SI for details).

In this paper we aim to investigate the influence of NP reorganizations under large deformation on mechanical reinforcement in PNCs followed by quenching for SAXS and TEM observations. A first remark on the deformation conditions is that here the duration of quenching, around 10 s, is shorter by one or even several orders of magnitude than the relaxation times necessary for rearrangement of particles aggregates at the relevant scales studied by scattering. Thus quenching should not induce fundamental differences and in situ measurements have been done on other systems [22,32] leading to very similar behaviors. The characteristic time of the deformation is the inverse of the gradient, $1/(0.005) = 200$ s, while the matrix terminal times at the deformation temperature, $T_g + 20$ °C, are more than 10 h. Therefore our measurements are not sensitive to the fact that chains are not cross-linked: we are in the entanglement regime as seen by previous Small Amplitude Oscillatory Shear (SAOS) measurements (using plate/plate rheology and DMA) [4,41]. Here we only focus on the NPs structural behavior (variation of SAXS and TEM images). Our basis will be the Nissan-St system and we will look at the effect of the filler network structure which we will vary by changing the NPs nature from Nissan to the larger NPs Ludox TM-40, initially dispersed in water and then transferred to the organic solvent (the smaller NPs Ludox LS show a behavior similar to the one of Nissan-St system, as can be seen in Fig. S6 in SI).

3. Results and discussion

In this paper we will also compare the results for PMMA matrix with the ones for a PS matrix ($M_w = 280$ 000, $I_p = 2$) where Nissan particles have been dispersed using the same method, as described in our previous work [4], and which have been studied using the same techniques. The results for the PS are shown in SI.
Fig. 2. SAXS scattering intensity of stretched Nissan Si/PMMA nanocomposites filled at 5%v/v from λ = 1 to λ = 3 in (a) parallel (||) and (b) perpendicular (⊥) directions. The insert in (a) shows a q^4 representation enabling some magnification of the shoulders signaling smoothened oscillations seen in I(q), under the form of apparent maxima in q^4. The black arrow indicates the unchanged position of the maximum at q ~ 0.04 Å⁻¹. (c) and (d) are the corresponding structure factors S(q) = I(q)/P(q) = S_{agg} × S_{inter} obtained by dividing the scattering intensity I(q) by the form factor of silica NPs, P(q), already measured [40]. In insert of (c) the evolution of peak position q* is plotted as a function of elongation ratio λ and scales as λ⁻³⁻⁰.⁵⁻⁰.⁵ in (||) direction (non-affine).

I(q) in the 0.001–0.01 Å⁻¹ is flat, which suggests that some aggregates of silica NPs of finite size are dispersed randomly in the polymer without additional organization at larger scales [41]. For stretched samples the SAXS scattering curves in || and ⊥ directions (Fig. 2a and b) can be described as follows. At high q, in both directions, the intensity is similar to that for isotropic case and exhibits a q⁻⁴ variation characteristic of the sharp interface between primary NPs and polymer. This behavior is independent of elongation ratio λ because, in that q-range, we are only sensitive to the form factor of the primary NPs, which are not deformed.

At intermediate q (~ 0.04 Å⁻¹), a shoulder is visible (Fig. 2a and b), which comes from the direct contact between particles [4]. Its position and amplitude remain unchanged in stretched samples in both directions (in the q^4 representation in insert in Fig. 2a, this shoulder transforms into a peak; the black arrow indicates the unchanged position of the shoulder). This is suggesting that the aggregates are not strongly modified, in particular not broken during deformation.

For lower q, 0.004 Å⁻¹ < q < 0.04 Å⁻¹, differences in I(q) appear under stretching. In perpendicular direction (⊥), the changes are weak with slightly lower values in intermediate q-range. In parallel direction (||), the changes are more visible: the intensity takes lower values for larger λ, with a slower increase and a flattening towards a plateau at lower q. These differences are more clear by plotting the structure factor S(q), as shown in Fig. 2c and d. The structure factor is obtained by dividing the scattering intensity I(q) by the form factor of silica NPs, P(q), which has already been measured (see reference [40]). If q could also be viewed as the product of the inter-aggregates structure factor S_{inter}(q) and the form factor of the aggregates P_{agg}(q). But the calculation of the S_{inter}(q) by dividing by the P_{agg}(q) can be delicate because the P_{agg}(q) can be modified under deformation due to orientation effects even without breaking. So we restrict ourselves to S(q), shown in Fig. 2c (||) and 2d (⊥). At high q, S(q), like I(q) does not change with λ. On the other side of this q window, for both directions and all elongation ratios λ, S(q) depends on q and varies as a power law q⁻¹. The value of this exponent is directly related to the effective fractal dimension Df of the aggregates, which is here equal to Df = 1.7 whatever the stretching directions and the elongation ratios. In between these two limits, at intermediate q, minima are observed at q ~ 0.026 Å⁻¹ with amplitude ~ 0.34. These minima and the slopes are the signature of the form factor of fractal aggregates composed of interacting primary silica NPs, i.e. P_{agg} ~ S_{intra-agg} × P(q) [32]. They remain unchanged with λ, showing that the internal aggregate structure is unchanged.

When decreasing q to even lower q, S(q) slightly flattens showing a shoulder (more pronounced at λ = 2 and 3) – before the final increase for q > 0 due to crazes. The corresponding abscissa of this shoulder q* increases with λ, which can be linked to a kind of concentration correlation size 1/q* or to a typical distance ξ = 2π/q* between aggregates. In (⊥) this q* is shifted to large q (smaller distances) for λ = 2 and the plateau is no longer well defined at λ = 3. In contrast in (||) the shoulder position q* decreases progressively with λ as λ⁻¹.⁰⁻⁰.⁵. This clearly differs from the affine deformation (q* ~ λ⁻¹). The non-affinity can be linked with (i) a non-affine shift of inter-aggregates structure factor S_{inter}(q) at low q, or (ii) the deformation and (iii) the orientation of the aggregates, the two latter modifying the P_{agg}(q). These three effects can combine together.

For a better understanding of such combination, SAXS measurements have been complemented with TEM images of the same samples in their quenched stretched state. Fig. 3 shows the
dispersed in another polymer matrix, polystyrene (PS), as reported without breakdown of their primary structure. The stretching leads to the displacement, rotation and orientation of the non-connected aggregates along the stretching direction (known from scratches, see Section 2). The aggregation number $N_{agg}$ and fractal dimension $D_f$ extracted from TEM analysis are $N_{agg} = 20$ and $D_f = 1.7$. These values are similar to the ones obtained for non-stretched samples ($N_{agg} = 27$ and $D_f = 1.6$) [41]. These TEM results are thus consistent with features in SAXS curves characteristic of the aggregates internal structure and shape: the $\lambda$-invariant position of the minimum, the unchanged slope values in intermediate $q$ and the value of the low $q$ plateau of $I(q)$. That confirms that aggregates do not undergo internal rupture ($N_{agg}$ constant with $\lambda$) and deformation ($D_f$ constant with $\lambda$). On the reverse, at lower $q$ we have seen that the abscissa $q^*$ of the $S(q)$ shoulder varies with elongation ratio $\lambda$; this variation is strong enough to indicate that the aggregates do not only orient but their centers of mass are also displaced.

Finally, we can conclude that at low silica volume fraction (5% v/v), the stretching leads to the displacement, rotation and orientation of the non-connected aggregates along the stretching direction without breakdown of their primary structure.

Similar experiments have been performed with the same NPs dispersed in another polymer matrix, polystyrene (PS), as reported in SI. Strikingly, the $S(q)$ profiles, shown in Fig. S2 are very similar.

![Fig. 3](image-url)

**Fig. 3.** (a) TEM images of Nissan-St/PMMA nanocomposites filled at 5%v/v and stretched at $\lambda = 3$ with a zoom in (b). The yellow arrow indicates the stretching direction determined thanks to the artefacts induced within the sample during the sectioning (crazing and creasing). The TEM analysis give a mean aggregation number $N_{agg} = 20$ and mean fractal dimension $D_f = 1.7$ with (c) an orientation of 114° compared to the x-axis (see Fig. S1 in SI for details). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

TEM, as shown in Fig. S3, evidence that aggregates also clearly orient along the stretching direction without breaking (radii of gyration and aggregate numbers are also shown, Fig. S4). Thus, at low silica concentration (5%v/v), the structural evolution of silica dispersion is similar for the same NPs in PS and in PMMA matrices.

This orientation effect seems independent of the nature of the matrix and is seen here, in our opinion, in one of the most clear-cut way in literature, for TEM in combination with SAXS.

### 3.1.2. Influence of NPs nature

Now let us discuss the influence of NPs nature and size on the structural evolution of silica dispersion state inside the PMMA matrix. From Nissan to Ludox NPs, one can expect some modifications on the final silica dispersion inside the matrix that can be due to the differences in the synthesis of the NPs. In particular, residual water can be present in the Ludox systems, which is known to provoke aggregation. Fig. 4 shows the $I(q)$ evolution for different stretching ratio from $\lambda = 1$ to $\lambda = 3$. Interestingly the structural evolution of the dispersion shows both similarities and differences with Nissan-St NPs. A similarity is that the NPs are forming primary aggregates inside the matrix whose morphology is close to the previous one ($N_{agg} = 13$, $D_f = 1.1$ instead of 1.7). The main difference is the presence of the low $q$ continuous increase of the intensity that suggests an additional aggregation level (secondary structure). The refined structure of this second level organization is still unclear but this can be the result of the presence inside the sample of a few number only of large scale objects. This low $q$ scattering is seriously affected by deformation in ($//)$ direction: at $\lambda = 2$ and $\lambda = 3$, a shoulder appears at low $q$ (instead of the continuous increase for $\lambda = 1$), revealing a correlation between the primary aggregates. This can be due (i) to the shift to low $q$ of the scattering of the large-scale structure, or (ii) to the rupture of the large-scale structure resulting in reorganization, displacement and shorter distances between the aggregates. A similar effect has been observed in other PNCs (silica-latex composite films) with increasing silica concentrations [42]. This is emphasized by plotting the structure factor $S(q)$ (see insert in (a)). But the latter emphasizes also the correlation hole (minimum), which becomes deeper in ($//)$ direction (from 0.63 at $\lambda = 1$ to 0.29 at $\lambda = 3$, indicated by the black arrow) and shifted at low $q$ by deformation. In ($\perp$) direction, the effect of stretching is clearly less pronounced and leads to very similar $S(q)$ in shape. This suggests that as previously observed for the Nissan-St case, the primary aggregate form factor is only slightly modified by the elongation: the objects can be elongated along the stretching direction (lowering of the fractal dimension) while keeping the same aggregation number. They are reoriented without breaking.

In summary, the effect of larger NPs with respect to Nissan-St is seen first through the different low $q$ scattering at rest due to different types of large-scale secondary aggregation. Then, under deformation the corresponding scattering is shifted at low $q$, modified by breaking or internal reorganization (elongation), parallel to the stretching.

### 3.1.3. Correlation with mechanical properties

We only focus here on the behavior in medium and large deformation at $T_g + 20$ °C, up to $\lambda = 3$. The behavior at low deformation (<1%) investigated by SAOS has been already detailed in our previous studies [4,41]. The measurements for PMMA PNCs filled at 5%v/v are presented in Fig. 5 with Nissan-St (red circles), Ludox LS (blue squares) and Ludox TM-40 (green triangles) silica with in insert a zoom from $\lambda = 1$ to 1.25. We also plotted the reference, i.e. polymer without silica, in dashed line. Obviously the stress is enhanced compared to the reference, but mostly at low deformation: the curves display higher stress and appear parallel to the reference one, and shifted by a constant
scattering intensity $S$ size and the nature of the polymer (PMMA or PS). This is consistent rather similarly in their mechanical response, whatever the NPs uniaxial stretching experiments. By us at their orientation as stretching proceeds (orientation is observed can also be attributed to a constant response of the aggregates to deformation, i.e. in the linear regime, we attributed the slight increase in reinforcement to possible increase of friction coefficient $S(q)$ obtained by dividing the scattering intensity $I(q)$ by the form factor of primary particles.

value of 0.14 MPa (see insert). This completely agrees with a similar shift of 0.12 MPa reported formerly for Nissan-St/PS NCs in similar conditions of temperature with respect to $T_g$ for non-grafted NPs [40] and for grafted NPs/PS PNCs [43]. At low deformation, i.e. in the linear regime, we attributed the slight increase in reinforcement to possible increase of friction coefficient through hydrogen bonds between PMMA and NPs [41]. It can also be attributed to a constant response of the aggregates to their orientation as stretching proceeds (orientation is observed by us at $\lambda = 3$ but can occur since the beginning of the deformation). Note here the low data precision at very low $\lambda$ in these uniaxial stretching experiments.

Finally, at low NPs volume fraction, all PNCs systems behave rather similarly in their mechanical response, whatever the NPs size and the nature of the polymer (PMMA or PS). This is consistent with the fact that silica primary aggregates are close in size and fractal dimension, and are both non-connected. It also means that the large aggregates giving low $q$ scattering are not relevant for mechanical properties. Under deformation, SAXS and TEM evidenced rotation/orientation of the primary aggregates along the stretching direction without breaking of their structure. As a consequence, apart from an initial moderate vertical shift, no significant effects of the stress—strain curves are observed; the filled matrix behaves as the unfilled one even at large deformation.

3.2. High NPs volume fraction

We will now see that the reorganization mechanisms are very different at high silica fraction. As above, we focus first on the example of Nissan NPs in PMMA.

3.2.1. Nissan-St/PMMA PNCs

Note that all SAXS measurements have been performed beyond the yield point, i.e. above $\lambda = 1.05$ (see mechanical data below). We start by the largest volume fraction, 20%v/v. The deformation is first evidenced by the 2D-SAXS scattering patterns also shown in Fig. 6 at different elongation ratios (from the top to the bottom: $\lambda = 1$, $\lambda = 1.5$, $\lambda = 2$, $\lambda = 3$). For $\lambda = 1$, $I(q)$ is isotropic. The SAXS pattern exhibits classical isotropic ring-shaped scattering related to the interaction between particles in the isotropic silica dispersion in the polymer matrix. Under stretching, SAXS patterns change from ring-shaped to elliptical and “butterfly” shapes at low $q$ (sample to detector distance of 10 m). Four spots can also be distinguished ($\lambda = 1.5$, and 2). After radial average treatment in parallel (a) and perpendicular (b) directions, and division by the form factor $P(q)$, the structure factors $S(q)$ for Nissan-St/PMMA PNCs filled at 20%v/v are shown in Fig. 6. The red (in the web version) curve is the example of Nissan NPs in PMMA. The network is the result of the progressive percolation of the primary aggregates, which form a continuous connected structure above a volume fraction threshold $\phi_c$. The inter-filler interactions revealed by the structure factor $S(q)$ can be reduced to the inter-particle interactions when the primary aggregates are small and ramified. Here, the typical expected homogeneity length scale is the one of the network mesh size. For the deformed case, the parallel scattering intensity

![Fig. 4. Scattering intensities for larger silica size, from Ludox TM-40/PMMA nanocomposites filled at 5%v/v, as a function of elongation ratio $\lambda$ in (a) (//) and (b) (\perp) directions. The inserts show the structure factors $S(q)$ obtained by dividing the scattering intensity $I(q)$ by the form factor of primary particles.](image)

![Fig. 5. Stress—Strain curves at $T_g + 20$ °C for PMMA nanocomposites filled with Nissan St (red circles), Ludox LS (blue squares) and Ludox TM-40 (green triangles) silica at 5% v/v. The dashed line represents the polymer reference without silica. In insert is shown a zoom of the same curves from $\lambda = 1$ to 1.25 which emphasizes the clear-cut vertical shift of the stress by 0.14 MPa, as compared to the unfilled one. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)
increases and the perpendicular one decreases leading to an elongation of the structure in the parallel direction and compression in the perpendicular one. Such variation of inter-particles distances results, in a domain of relatively high concentration, in butterfly patterns [12,13,29,28]. We followed the evolution of the $S(q)$ peak position $q^*$ as the function of $l$ and one obtains $q^*_\parallel \sim \lambda^{-0.9 \pm 0.05}$ in parallel and $q^*_\perp \sim \lambda^{0.5 \pm 0.05}$ in perpendicular (see inserts in Fig. 6a and b). These two variations are very close to affine deformation which gives $q^*_\parallel \sim \lambda^{-1}$ and $q^*_\perp \sim \lambda^{0.5}$. Thus, we can infer that at 20%v/v the silica structure is displaced affinely with the macroscopic deformation.

Similar observations (four spots pattern) have been reported in numerous cases of heterogeneous systems at high concentrations [22,26]. As said above, at first glance, the butterfly patterns results from the fact that the aggregates deformation is much weaker than the inter-aggregates distance deformation. The latter can be non-affine or affine, as explicitly reported for polyurethane elastomers composed of highly connected hard domains [19].

Now we turn to some intermediate concentrations: 10% and 15% v/v, for which we performed similar analysis. The results are reported in Fig. 7 (and the 2D patterns can be shown in Fig. S7 in SI). It shows the evolution of the peak position $q^*$ as a function of $l$ in parallel and perpendicular directions for 10%, 15% and 20%v/v. In parallel direction, the $q^*$ scales as $\lambda^{-0.3 \pm 0.05}$, $\lambda^{-0.4 \pm 0.05}$ and $\lambda^{-0.9 \pm 0.05}$ for 10%, 15% and 20%v/v, respectively. In perpendicular direction, $q^*$ scales as $\lambda^{0.5 \pm 0.05}$. Hence the structure deformation deviates from the affinity in parallel direction when the silica volume fraction decreases while it remains always affine in perpendicular direction. One can suggest that the deviation can be related to the proximity of the percolation threshold for which we can have coexistence between isolated aggregates and filler network. As a result, we observed an intermediate behavior under deformation between the non-affine variations of the non-connected aggregates highlighted for the diluted case and the affine deformation of the pure 3D network observed at 20%. In other terms we can also say that the network below 20% is not homogeneously connected.

Note that we also performed TEM imaging on 20%v/v PNCs stretched at $l = 3$. However, because of the high silica concentration, it appeared difficult to appreciate the deformation effect on these samples and thus quantify the silica displacement (see the TEM image of the stretched samples in Fig. S8). Scattering is much more sensitive in the concentrated case.

Concerning the same Nissan-St NPs, the PMMA PNCs can also be compared to PS PNCs since they have also been investigated in the
concentrated regime. However, samples with 20% NPs did not accept large deformations, the modulus being too high, so the largest fraction studied was 15%. The stress—strain curve, formerly reported [4], displayed a large maximum of stress around $\lambda = 1.1$, accompanied by unambiguous signs of shear bands (not placed in the beam). We show in SI these results only as an example of saturation effect. The $S(q)$ (Fig. S5 and comments in SI) show in (//) direction a strong saturation effect as soon as $\lambda = 1.5$, up to 6, and in (\perp) a non monotonous variation of the shoulder abscissa (first increase as usual, then decrease). Indeed, we are far from the situation where NPs displacements can be affine.

### 3.2.2. Influence of NPs nature

We compare here the results presented above to the Ludox TM-40/PMMA nanocomposites, the stress—strain evolutions as a function of silica volume fractions (10%/v, 15%/v and 20%/v). At low $\lambda$, the curves exhibit an increase of stress (vertical shift). This shift increases with increasing the volume fraction (i.e. the connectivity). This agrees with earlier findings in PS where it was found that this effect is correlated to the formation of filler network [40]: the more connected the higher the stress shift. Then, around $\lambda = 1.05$, all curves exhibit a yield point (i.e. reduction of the slope of the curves) more pronounced at 20%/v, above which a clear change in stress evolution is observed. These yield points can be linked to a percolating structure [44] in the systems, suggesting that silica arrange in this range of concentration as a network which is broken under deformation. For larger $\lambda$, the stress goes on increasing following a linear evolution quasi-parallel to the one of pure PMMA for 10%, like at low silica fraction. But for 20%, it backs towards to the one of the unfilled polymer (the slope after the yield is clearly weaker for 20% than for 10%/v).

Fig. 10 compares, for the largest volume fraction 20%/v, the Nissan-St/PMMA stress—strain curves with the ones for Ludox LS and Ludox TM-40 PMMA NCs. For comparison we also plotted the stress of the unfilled PMMA (dashed line). Each curve exhibits a vertical shift at low $\lambda$ followed by a yield point. It is more pronounced for small NPs (Nissan-St and Ludox LS), which is a first difference explained by a larger connectivity. The other difference is that, meanwhile the stress in Nissan-St systems recovers the stress of the pure matrix at $\lambda = 3$, the stress curve for the two others systems remains parallel to the one of pure polymer, with a shift of about 1.27 MPa. We recall at this stage that, this shift effect was also observed formerly for Nissan-St in PS, with similar orders of magnitude up to 10% [40]. For different polymer $M_w$ from 138,000 to 1,777,000 g/mol, the matrix and filled material curves depended on $M_w$ but not the shift which was found constant (while depending on the distance to glass temperature, $T - T_g$ [40], and on the deformation gradient, $d\lambda/dt$, sec$^{-1}$). We attribute these observations to NPs reorganizations inside the polymer after the yield point, at which the reorganization of the connectivity starts.

As shown by the SAXS data, non-affine deformation is present in all considered systems with constant “vertical shift” of the stress (Ludox LS/PMMA, Ludox TM-40/PMMA and Nissan-St/PS). The fact that the filler structure gives a stress contribution up to very large deformation is consistent with progressive rearrangement, or progressive breakdown of parts of the network into smaller pieces.
which can extend to large deformation in case of network structural heterogeneity. To this stress is added the stress due to the polymer matrix, which builds up under deformation. The fact that the slope of the stress curve is close to the one of the pure polymer implies that the network contribution is constant.

In contrast, affine deformation is only seen in the case of Nissan-St/PMMA (20%) which presents a less persistent reinforcement, since the stress—strain curve reaches the behavior of the unfilled polymer at large deformations. One can explain affinity in this range of large deformation (i.e. above the yield point) by having, initially, a more homogeneous network, which breaks in many small parts of similar size, the interactions of which decrease with deformation because they separate more and more. They are then embedded in the matrix and displaced following the macroscopic deformation and most of the stress is due only to the matrix. As a consequence, the stress returns to the value of the pure polymer at large deformation. When decreasing the silica volume fraction a deviation from affinity is observed (Fig. 7) leading to slower stress decrease (Fig. 9).

Thus the major mechanical difference between the systems comes from the structural consequences of the network breakdown influenced here by the NP–NP interaction. Comparing PS and PMMA filled with Nissan-St at high volume fraction, the stronger the interaction between NPs (as in PS) the more heterogeneous the structure of the broken network, the less affine the deformation and the more constant the stress shift. Then, by comparing Ludox and Nissan-St in PMMA, one may propose that the presence of residual water in Ludox systems during the preparation modify the NP–NP and PMMA-NP interactions [45], leading to stronger NPs attractions. Note that the PMMA can strongly interact with the NP surface through hydrogen bonds between silanol groups on silica and PMMA ester groups.

To sum-up the structural affinity or non-affinity after yielding is associated to the NP–NP interaction. If this interaction is weak the deformation induces a gradual network breakdown decreasing the stress. On the contrary, if the NP–NP interaction is strong (due to athermal interaction between the NPs and the polymer for PS systems or to the presence of residual water during processing in PMMA systems) the network breakdown leads to the formation of heterogeneous structures and a stress evolution similar to the pure matrix. The network breakdown and following NPs reorganization

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**Fig. 8.** Structure factor \( S(q) \) for Ludox TM-40/PMMA PNCs filled at 20%v/v and stretched at different elongation ratios \( \lambda \) in (a) \( (//) \) and (b) \( (\perp) \) directions.

**Fig. 9.** Stress/Strain curves for Nissan-St/PMMA nanocomposites filled with 10% (blue circles), 15% (green squares) and 20%v/v (red triangles). The dashed line represents the pure PMMA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 10.** Stress—strain curves of PMMA nanocomposites filled at 20%v/v with Nissan-St (red circles), Ludox LS (blue squares) and Ludox TM-40 (green triangles). The dashed line corresponds to the unfilled PMMA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
are dependent of interaction strength between NPs. For instance, the grafting of PS chains at the silica surface yields to softer NPs interaction increasing the network deformability and thus lowering the reinforcement [43].

3.3. Extension/contraction cycles: evidence of irreversible deformation

Fig. 11 reports the stress–strain cycles, again in our example of Nissan-St/PMMA PNCs filled at 0%v/v (a), 5%v/v (b) and 20%v/v (c). For unfilled polymer (0%v/v), the initial length is recovered: the stress–strain curves are identical for each cycle, after a slight delay just at the end of the return, before the recovery of initial state. Therefore, the Young modulus $E$ (i.e. the initial slope of the curve) for each beginning of cycle is similar (around 2.5 MPa, see insert). Note that this is also a simple proof that the polymer matrix is in a regime of elastic deformation, which complements our former justification. For filled systems, at both concentrations (5% and 20%v/v) after one cycle, the system shows residual deformation: the stress returns to 0 but the initial length is not recovered. The higher the silica concentration, the larger the residual deformation: $\lambda_{\text{res}} = 1.2$ at 5%v/v and $\lambda_{\text{res}} = 1.6$ at 20%v/v. When the first cycle is achieved, the two following cycles display similar behavior with equal stress and residual deformation. This suggests that irreversible phenomena arise during the first cycle with no additional effects during the next ones. The second and third curves remain below the unfilled one, which they recover at large $\lambda$. This effect is common to both 5% and 20% silica volume fractions. The evolution of the initial slope is on the reverse different for the two volume fractions. For 5%v/v, i.e. in the non-connected aggregates dispersion, since the second and third stretching curves start from a larger length, their initial slope is only apparently larger than for 0%; taking this new length as a reference, the apparent Young modulus (low $\lambda$) remains quite unchanged for all cycles. For 20%v/v, i.e. in the network regime, the initial slope shows a strong decrease by a factor 2.9 between the first and the second cycle. This results, for the first extension, in the vertical shift described above, which vanishes for cycle 2 and 3. To better understand this mechanical response let us follow the evolution of the silica dispersion state during extension/retraction cycles.

Fig. 12 presents the SAXS scattering patterns obtained at different times of the cycles for 20% silica. First, as usual at rest (a), i.e. before deformation, the patterns present circular ringed shape of isotropic network dispersion (the ring position is related to the mesh size of the network). Second, as usual also at $\lambda = 2$ (b), as described before, the patterns become anisotropic with butterfly shape, four spots are also visible. Third, strikingly, when the stress comes back to zero (c), the SAXS pattern does not recover its initial ring shape but is clearly anisotropic, with four intense spots and “inversed” butterfly shape (i.e. the axes are rotated by 90°). The above observations suggest that, during return to $\sigma = 0$, the deformed structure reach an isotropic state before $\lambda = 1$, and becomes then compressed in (/\) direction and stretched in the transverse one, which is responsible of the inversion of the butterfly axes (see scheme of Fig. 12). Note that after two more cycles (d) the SAXS patterns keep the same shape.

The network breakdown is clearly evidenced by stress–strain isotherms (Fig. 11) in extension/contraction cycles: when the stress after one first deformation cycle come back to zero, the initial length is not recovered: residual deformations are thus observed at zero stress. The existence of aggregates rearrangements could explain the phenomenon. Indeed SAXS measurements reveal that scattering patterns before and after first cycle are clearly different (Fig. 12). Anisotropy remains present at zero stress: it can be associated to filler rearrangements during the retraction leading to the plasticity. Note that scattering patterns after 3 cycles are identical to the one of the first cycle (with however slightly less intense spots), as well as the stress–strain curves, suggesting that phenomena occurring at the first elongation are irreversible and
not present after. This plasticity effect depends on silica volume fraction. Long et al. [46] have studied the relaxation and the residual deformations in filled systems after deformation by simulations. They proposed two mechanisms. In a first step, at high volume fraction, connectivity between fillers creates an energetic barrier that impedes the local topological rearrangement: the affine deformations of the network should be favored. In a second step, when the energy stored in deformation is too high, these barriers are passed; when the applied tensile stress is reduced again, it is not possible for the system to come back to initial structural state, leading to the development of residual deformation (this effect is magnified for higher filler volume fraction). This scheme is consistent with our experimental observations. Passing the barriers would correspond to the yield point. However, after the network breaking the displacement of the different pieces of the broken network can be either non-affine — as predicted, if they still interact strongly, or just simply follow the displacement of the points of the matrix and become affine; this depends on their spatial organization and on the response of this structure to the deformation.

4. Conclusions

In this paper we investigated the structural evolution of silica dispersion state under deformation above \( T_g \) in model silica/PMMA nanocomposites (PNCs) by a combination of Small-Angle X-ray Scattering (SAXS) and Transmission Electronic Microscopy (TEM) as a function of silica volume fraction. The silica reorganizations can be well characterized and correlated with the mechanical response. At low silica volume fractions and for all PNCs systems, the reinforcement is low and rotation/orientation of non-connected aggregates along the stretching direction without breaking of their structures is observed. At high volume fraction, all stress—strain curves exhibit near change of slope followed by a yield point. This result is associated with the breakdown of the silica network. The latter is clearly highlighted by additional cyclic deformation experiments. Above the yield point, affine or non-affine deformations are observed depending on the nature of the particle (Nissan-St or Ludox) or of the polymer and are related to the different structures formed after yielding. A correlation can be found with mechanical behavior: above the yield point the curves looks like the matrix one plus a constant shift in case of non affine deformation, while in case of affinity the shift vanishes at large deformation. We propose that the affine displacements can be associated to the breakdown of a network in pieces of similar sizes, which follow at larger deformation the matrix in which they are embedded, while the non-affine displacements can be associated to a breakdown in more heterogeneous structures which go on interacting at larger deformation. Such nature of network breakdown might be controlled by the strength of NP—NP interactions.

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Appendix A. Supplementary data

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References