Experimental Report

02/06/2014

Proposal:	**9-12-317**	**Council:**	4/2012

Title: Chains conformations in nanocomposites with controlled aggregation: effect of the polymer-silica size ratio.

This proposal is resubmission of: 9-12-306

Researh Area: Materials

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Samples:
$(C_5H_5D_5O_2)_n$
Silica

Instrument	Req. Days	All. Days	From	To
D11	2	2	23/02/2013	24/02/2013
			05/07/2013	06/07/2013

Abstract:

The impact of the chain-filler size ratio on chain extension in nanocomposites is controversial. Discrepancies measured in previous experimental studies can be ascribed to the filler dispersion and the difficulty to isolate the chain signal in SANS experiments. The aim of our project is to study polymers conformations in nanocomposites with controlled aggregation as function of the polymer-silica size ratio using optimized silica matching conditions.

Chains conformations in nanocomposites with controlled aggregation: effect of the polymer-silica size ratio.

The aim of the experiment was to measure the polymer chain signal in nanocomposites made from colloidal silica and nanolatex casting. The study was performed during two experimental runs. The first run was dedicated to study of the conditions (matching strategy, annealing of samples) required to measure a chain signal in such samples. In the second run, various nanocomposites formulated with different colloidal silica (Ø=10 nm and 28 nm) and polyethyl methacrylate (PEMA) chains (Mw= 20 000g/mol and 100 000g/mol) were investigated. In both sessions, samples were measured using three configurations (resulting q-range: 1.10^{-3}-0.3 $Å^{-1}$).

Run 1: Two strategies were studied to measure chain conformation in solid samples filled with silica nanoparticles:

(1) H-chains (5%) diluted in a H-D copolymer matching silica nanoparticles.
(2) Mixture of H- and D-chains fulfilling the zero average contrast conditions (ZAC).

As samples are prepared from latex beads made of one type of chain (H or D or H-D copolymer), before the annealing of solid samples the latex bead signal is predominant. Hence, two kinds of annealing were studied to promote latex bead dissolution:

(a) Thermal annealing under vacuum (120°C, or 150°C, or 180°C, for 1 week or 3 weeks)
(b) Solvent annealing followed by drying under vacuum (Methyl Ethyl Ketone (MEK) vapors, or a mass of liquid MEK (two masses tested) put on the sample stored in a saturated atmosphere for one week)

These studies were performed on matrices and nanocomposites (10% v/v) formulated casting a colloidal solution made of PEMA latex (R_{latex}=23 nm, Mw=100 000g/mol) and colloidal silica Ludox TM 40 (R_{Si}=28nm).

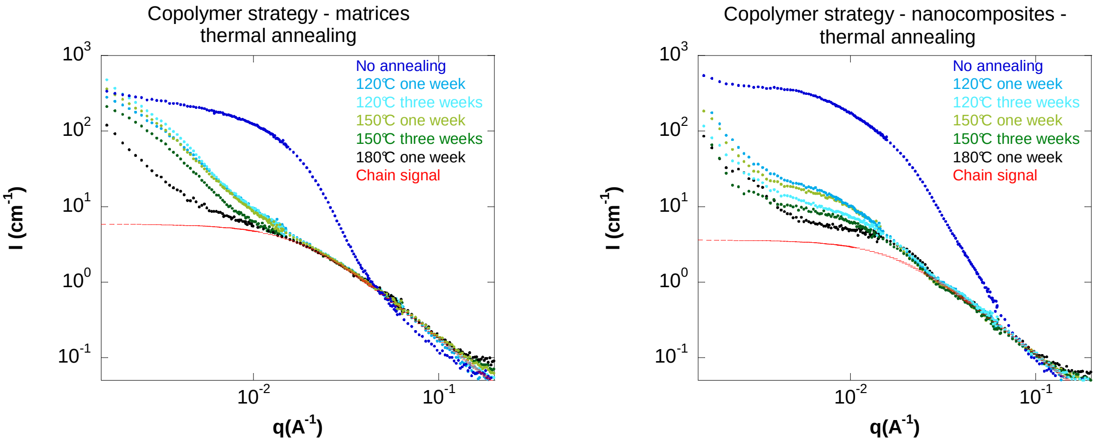

Figure 1: (left) Copolymer matrices with 5% of H chains for different thermal annealing (right) Copolymer matrices with 5% of H chains and 10% of silica nanoparticles for different thermal annealing. Red curves: the Guinier form factor for Rg=90Å.

Using the copolymer strategy (figure 1), the chain signal was correctly measured in the high q range for thermally annealed unfilled samples, despite of an increase of the signal at low q. The contribution of this low q signal is decreased with the annealing temperature, but remains for 180°C annealing. For nanocomposites, a contribution of silica appears around 2.10^{-2} $Å^{-1}$. Bad matching is highlighted in spite of the correct matching of copolymer and silica particles scattering length densities ($\rho_{Copo}=3{,}4.10^{10}$cm $^{-2}$ and $\rho_{Si}=3{,}5.10^{10}$cm $^{-2}$ according to contrast variation experiments). This sensitivity can be explained by the low intensity of the chain signal (about 10 cm^{-1}). This low intensity is inherent to the strategy which uses a low content of H-chains to avoid the contribution of a chain structure factor to the signal.

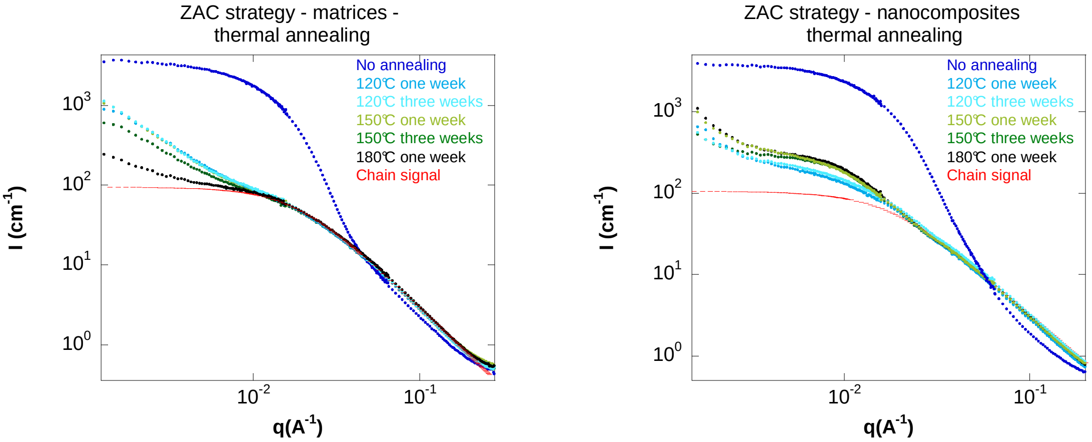

Figure 2: (left) H/D matrices for different thermal annealing (right) H/D matrices with 10% of silica nanoparticles for different thermal annealing. Red curves: the Guinier form factor for Rg=90Å.

Using the ZAC strategy (figure 2), the chain signal was correctly measured until 10^{-2} Å^{-1} in matrices, with an important intensity (10^{2}cm^{-1}), and like for the previous strategy, the thermal annealing decreases the low q contribution. For filled samples, the chain signal is disturbed at low q and can be explained by the H/D ratio which is not optimized in our samples. Indeed, the scattering length density of D-chains evolved compared to our previous batch (7.4.10^{10}cm^{-2} instead of 5.6.10^{10}cm^{-2}). Moreover, the silica contribution increases with annealing. The contrast seems amplified with thermal annealing and could be due to degradation products accumulated at the polymer-silica interface.

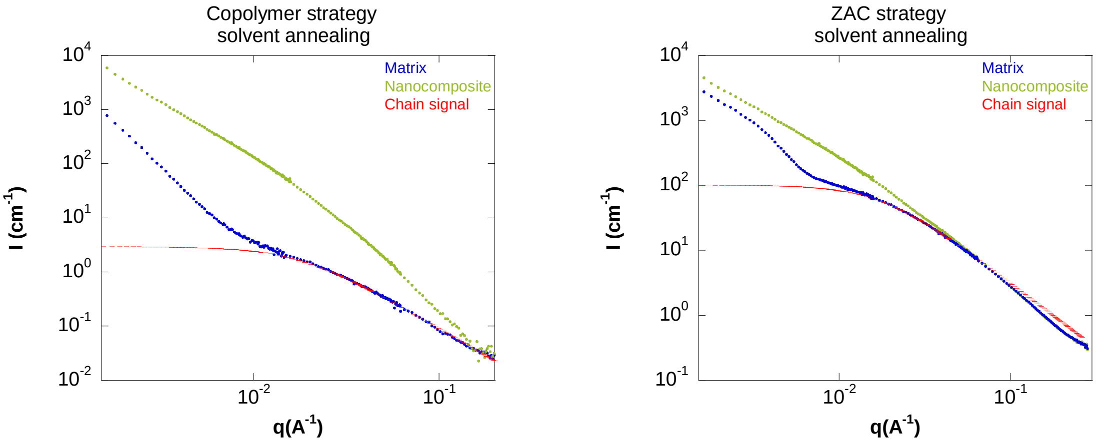

Figure 3: (left) Copolymer samples solvent annealed (right) H/D samples solvent annealed. Red curves: the Guinier form factor for Rg=90Å.

Solvent annealing was investigated for both silica matching strategies (figure 3). SANS spectra are similar for the different solvent annealing conditions. Whatever the strategy used, the chain signal was correctly measured in matrices in the high q range, but with silica nanoparticles the signal is dominated by another contribution. As this contribution is different to one observed for thermal annealing, we suppose that samples were not perfectly dried in presence of silica, organic solvent molecules could remain into samples.

According to these results, in order to measure chain signal in our nanocomposites, we chose to use the ZAC strategy adjusting the H/D ratio according to the scattering length density measured for D chains. The thermal annealing of samples at 120°C for one week was selected to insure latex bead dissolution.

Run 2: Nanocomposites prepared with different contents of silica nanoparticles were investigated. Two kinds of silica nanoparticles: Ludox TM40 (Ø=28 nm) and Ludox SM30 (Ø=10 nm), and two lengths of polymer chains: PEMA 100 000g/mol and PEMA 20 000g/mol, were used to formulate nanocomposites. In all cases, the polymer was synthetized and used in the latex form which had a characteristic bead size about Ø=25 nm.

For nanocomposites made of PEMA 100 000g/mol the chain signal appears at high q with the characteristic q^{-2} slope of the Debye form factor (figure 4).

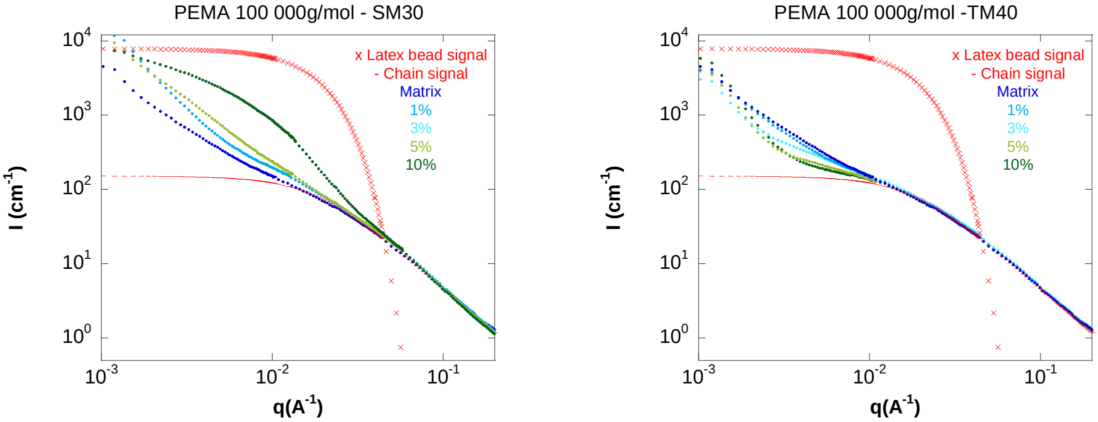

Figure 4: PEMA 100 000g/mol nanocomposites annealed for 1 week at 120°C (left) SM30 nanoparticles filling (right) TM40 nanoparticles filling. Red symbols display calculated chain signal (Rg=90Å) and latex bead signal.

At lower q a contribution evolving monotonously with the silica content is observed. Surprisingly, this evolution appears in the opposite way for both kinds of silica nanoparticles. For SM30, the low q contribution increases with the silica content and was previously attributed to partial dissolution of latex beads in presence of silica particles [1]. For TM40, the low q contribution decreases with the silica content and can be attributed to an improvement of latex bead dissolution with bigger silica particles. The difference of behavior between SM30 and TM40 nanoparticle could be ascribed to the size ratio between silica and latex particles. With TM40, the size ratio is about 1, there is not confinement of latex beads, contrary to SM30 particles ($R_{Latex}/R_{Si}=2.5$) that can embed latex particles and prevent their dissolution.

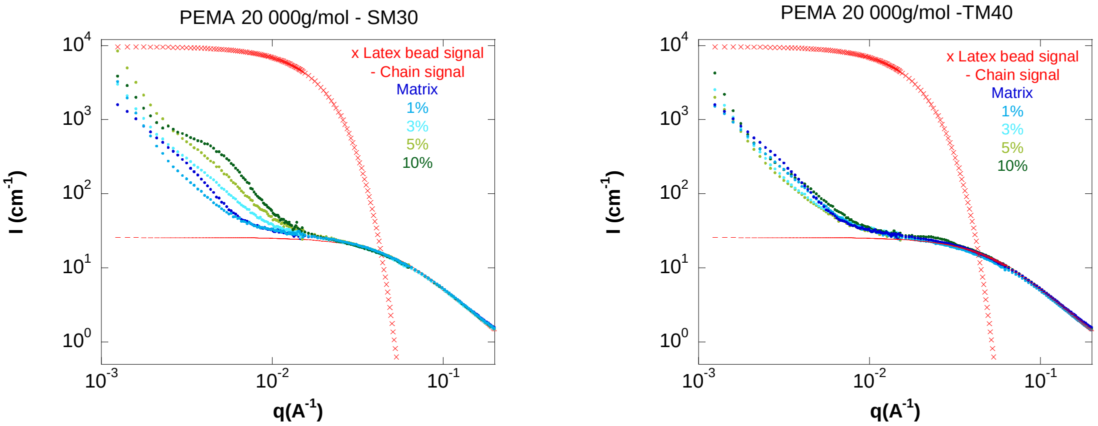

Figure 5: PEMA 20 000g/mol nanocomposites annealed for 1 week at 120°C (left) SM30 nanoparticles filling (right) TM40 nanoparticles filling. Red symbols display calculated chain signal and latex bead signal.

For nanocomposites made of shorter polymeric chains, PEMA 20 000g/mol, enhanced chains mobility is expected. (This mobility favors the formation of small silica nanoparticles aggregates [2]). The signal is identical for all silica fractions in TM40 nanocomposites, suggesting a total dissolution of latex beads whatever the filler content (figure 5). Below 10^{-2} Å^{-1}, a power law with an exponent 2 is observed. This evolution can be compared to polymeric gel scattering profiles [3], and could be attributed to concentration heterogeneities of H and D chains. For SM30 nanocomposites, the filler content has an impact on the intermediate q range: intensity increases with silica fraction. This behavior is comparable to the one observed in PEMA 100 000g/mol – SM30 nanocomposites. However, the difference between the latex bead signal and the 10% nanocomposite signal appears less important in PEMA 20 000g/mol nanocomposites than in PEMA 100 000g/mol. It suggests a better dissolution of latex beads in nanocomposites made of shorter chains, which is consistent.

In conclusion, the radius of gyration of polymer chains in nanocomposites is not modified by silica nanoparticles. However, the filler impacts the latex bead dissolution, and opposite behaviors were observed for different size ratios of latex and filler.

[1] Tatou et al, Macromolecules, 2012, 45, 1663–1675. [2] Banc et al, Macromolecules, 2014, 47, 3219-3230. [3] Bastide et al, Macromolecules, 1988, 21, 2469-2651.