Chain Response to Deformation, Filler Displacement, and Mechanical Reinforcement in Polymer Nanocomposites

F. Boué[1], N. Jouault[1], C. Chevigny[1], J. Jestin[1], S. Said[2], P. Vallat[1], F. Dalmas[3], R. Schweins[4], E. di Cola[5], D. Gigmes[6], D. Bertin[6].

[1] *LLB, CNRS_CEA-IRAMIS, CE Saclay, 91191Gif-sur-Yvette, Cedex, France*

[2] *Polymères, Propr^és aux Interfaces et Composites, Univ Bretagne Sud, Rue St Maudé, BP 92116, 56321 Lorient, France*

[3] *Inst. de Chimie et des Matériaux Paris-Est, UMR 7182 CNRS / Univ. Paris-Est, 2 rue Hi Dunant 94320 Thiais France*

[4] *Institut Laue Langevin DS/LSS, 38042 Grenoble Cedex 9, France*

[5] *European Synchrotron Radiation Facility ESRF, 6 rue Jules Horowitz, BP 220, 38043 Grenoble, France*

[6] *Lab. Chimie Provence, UMR 6264, CNRS - Univ. Aix-Marseille, St Jérôme, case 542, 13393 Marseille Cedex 20 France*

Our aim is to relate the mechanical reinforcement in polymer melts containing nanoparticles (NP)(as a model for nanocomposites, including the case of filled rubber) to the structure of the NP dispersion, at rest and under deformation, and the chains deformation.

We synthesized by ourselves model nanocomposites with dispersion of nanoparticles at the level we want, i.e. non aggregated, or partially aggregated in clusters of various compacity/fractalness, and various degree of connectivity. Then we can understand the different components of the so-called "nanoeffect" in reinforcement. We used two routes:

- a controlled grafting leads to single particles in solution which can be characterized as made of an individual core and a polymer corona (Chloé Chevigny, Ph. D, and [1], [3]). These particles can be dispersed in a polymer matrix in various state of aggregation, individually dispersed or in lumps depending of the matrix used. This is characterized using both SAXS and TEM (Figure 1 left), in isotropic state as well as under stretching. We can observe how much these arrangements are deformed, and their relation with reinforcement. Further more, we can also, using SANS and deuteriation, observe the behavior of the corona, under the effect of the matrix and of the deformation.

- a direct dispersion through solvent evaporation, leads to homogeneously dispersed fractal aggregates, allowing control of inter-aggregate distances, as shown by TEM and SAXS and SANS (Nicolas Jouault, Ph. D, [2]). The global Tg shift is weak. At low concentration, the increase in elastic modulus is strong, even at low silica fraction in the non connected range(5%). Were it due to "slowed down" regions around or between particles, they would have sizes > several tens of nm, 10 times larger than values proposed from fits of mechanical measurements or extrapolated from high T NMR.

Striking results are obtained from deuterated chains under deformation: the grafted chains are deformed like the matrix ones. Would they be "slowed down", this has no effect under deformation. Similarly, labeled chains inside the matrix deform exactly as in the non reinforced system (Figure 2)! There is no influence of slowing down, or other interfacial or confinement phenomenon.

Then, reinforcement at large deformation can be decomposed in a filler fraction independent chain contribution, increasing with λ, and an aggregate related one, which is **practically constant** with deformation. This suggests progressive rearrangement of particles when they hit, analogous to buckling.

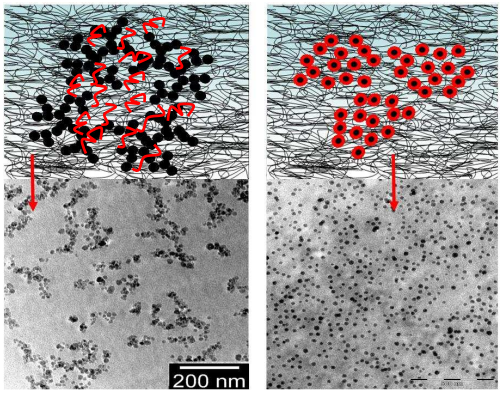

Figure 1: Electronic microscopy (TEM) and schemes of nanocomposites. Left: polymer matrix, deuterated chains (red) and nanoparticles of silica (black) in ramified aggregates. Right: same matrix, particles grafted with chains (which can be deuterated, red) before dispersion.

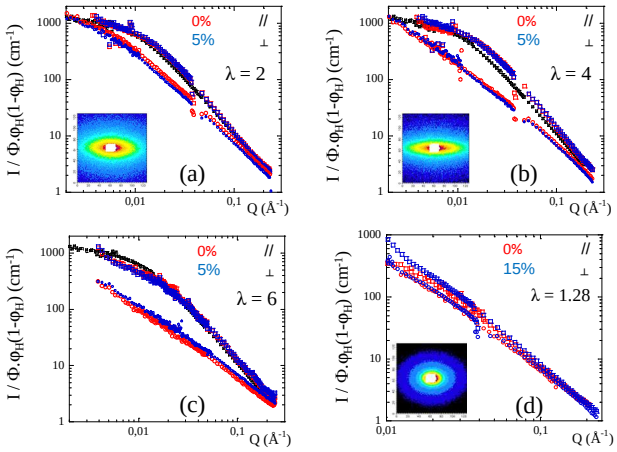

Figure 2: Comparison of chain deformation between unfilled polymer (red) and nanocomposites (blue).: SANS (log-log) of deformed chains in pure polymer and filled with 5%v/v (blue curves) in directions // (O) and⊥ (□) to stretching for elongation ratios λ=2 (a), 4 (b), 6 (c).

References

1. Chevigny, C. ; Gigmes, D. ; Bertin, D. ; Jestin, J. ; Boué, F. *Soft Matter*, **2009**, *5(19)*, 3741-3753
2. Jouault, N. ; Vallat, P. ; Dalmas, F. ; Said, S. ; Jestin, J. ; Boué, F. *Macromolecules*, **2009**, *42*, 2031-3040.
3. Chevigny, C. ; Gigmes, D. ; Bertin, D. ; Jestin, J. ; Schweins, R., Di-Cola, E. ; Dalmas, F. ; Bertin, Boué, F. *Macromolecules*, **2010**, *43*, 4833-4837.