Molecular motions of statistical copolymers at the interfaces with inorganic filler particles

The dispersion of inorganic filler nanoparticles within a polymer matrix may result in a significant enhancement of some of its mechanical properties, such as the Young modulus. Recent studies have led to a better understanding of the underlying reinforcement mechanisms. In particular, the role of the structures formed by the inorganic filler nanoparticles on the increase of the Young modulus is now well-captured. The contribution related to the change of the chain dynamics located at the interfaces with the filler nanoparticles has also been investigated, though this question still remains open. Most of the above-mentioned works were carried out on model materials composed of one homopolymer and a given kind of inorganic filler nanoparticles displaying attractive interactions with the polymer chains. However, from an applicative point of view, many commodity polymers display weak or even repulsive interactions with the surface of inorganic fillers such as silica or clays, thus limiting their dispersion within the polymer matrix. A possible strategy to circumvent this difficulty relies on the use of compatibilizing agents such as statistical copolymers. Though scarcely addressed from an experimental point of view, the behavior of such copolymer chains in the close surrounding of the filler particles is a key feature to get a better understanding of the evolution of the Young modulus of these nanocomposites.

The goal of this PhD thesis is to investigate the behavior of statistical copolymers poly(A-stat-B) within nanocomposites composed of silica. The units B of such copolymers will display attractive interactions with the surface of the filler particles whereas the units A will be hydrophobic. The conformational behavior of such copolymer chains and their local structuration in the vicinity of the interfaces will be first investigated and, in particular, the influence of the copolymer composition as well as the distribution of the A and B units along the chains (microstructure). The evolution of the local concentration in A or B units will be monitored as a function of the distance from the interfaces with the filler particles. Such information will be derived, in particular, by solid-state NMR. In a second step, the dynamical behavior of the copolymer chains at the interfaces will be probed and a peculiar attention will be paid to the segmental motions related to the glass transition. From an experimental point of view, such information will be derived by means of solid-state NMR and broadband dielectric relaxation spectroscopy. These experimental data related to the local dynamics will be compared to the predictions of recent numerical simulations describing such kinds of composites and will be used to get a better knowledge of the mechanisms involved by the mechanical reinforcement of such materials.