Poster abstract

P.05 **Dynamical behavior of interfacial polymer chains in nanocomposite hydrogels: A solid-state NMR approach**

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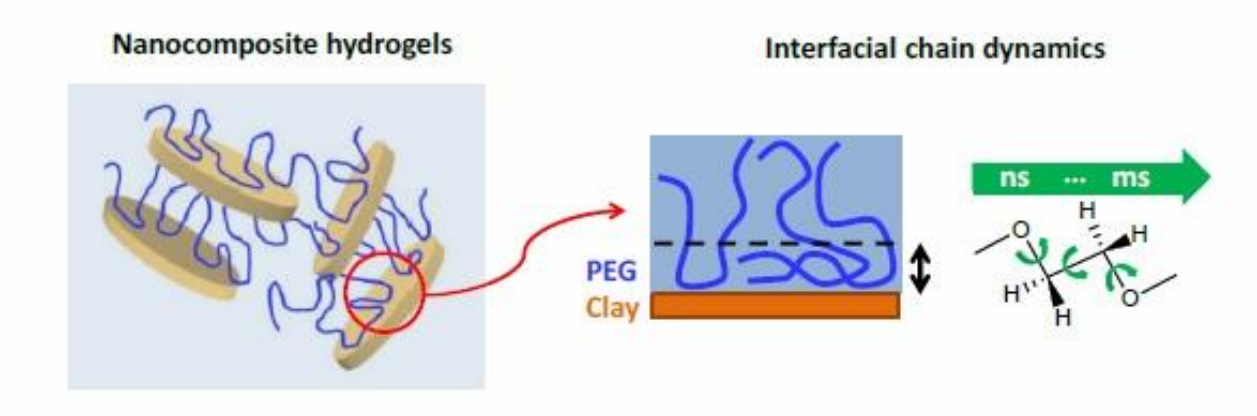
In contrast to bulk polymer matrices reinforced by nanosized inorganic fillers, the design of nanocomposite hydrogels is quite recent since the first contribution along this line was reported by Haraguchi et al. in 2002 [1]. The molecular origins of the mechanical reinforcement induced by adding clay layers *within polymer hydrogels* have not yet been extensively investigated. In such systems, the progressive growth of clay platelet aggregates leads to a connected structure, the so-called "house of cards" structure. As a result, part of the polymer chains are constrained between both faces and edges of the clay layers. Similarly to the case of filled bulk polymer matrices, the local dynamics of such interfacial chains is a key feature to get a better description of the reinforcement of the Young modulus displayed by these hybrid hydrogels.

In the present work, hydrogels composed of poly(ethylene glycol) (PEG) chains and Laponite were considered. Combined solution and solid-state NMR approaches were used to probe the segmental dynamics of the PEG chains adsorbed on the clay platelets, over the nanosecond to millisecond time scale. In a first step, the time evolution of the PEG chain dynamics during the hydrogel formation was investigated. In particular, the level of local constraints undergone by the PEG chains was monitored and this description at the molecular length scale was correlated to the variation of the rheological behavior related to the gelation phenomena. Such comparisons demonstrated that the slowing down of the segmental motions arises from adsorbed PEG repeat units or chain portions strongly constrained between aggregated clay layers. In a second step, the segmental dynamics of these interfacial PEG chains was investigated through ^{1}H, ^{2}H and ^{13}C solid-state NMR spectroscopy. These constrained PEG repeat units, though frozen over a few tens of nanoseconds, were found to display significant reorientational motions over the tens of microseconds time scale. The question of the characteristic motional frequencies as well as the motional geometry of such PEG chains was then investigated in details [2].



[1] K. Haraguchi, T. Takehisa; "Nanocomposite Hydrogels: A Unique Organic-Inorganic Network Structure with Extraordinary Mechanical, Optical, and Swelling/De-swelling Properties", Adv. Mater. (2002), 14, 1120

[2] C. Lorthioir, M. Khalil, V. Wintgens and C. Amiel; "Segmental Motions of Poly(ethylene glycol) Chains Adsorbed on Laponite Platelets in Clay-Based Hydrogels: A NMR Investigation", *Langmuir* (2012), 28, 7859