

## PhD Proposal 2019

UNDERSTANDING OF 'PLASTICIZER EFFECT' : CONCENTRATION FLUCTUATIONS AND BROADENING OF THE GLASS TRANSITION IN DYNAMICALLY ASYMMETRIC MIXTURES OF INTEREST FOR TIRE FORMULATION.

### Collaboration research project

Materials Physics Center, University of the Basque Country, San Sebastian, Spain

Michelin, Research & Development Center, Clermont-Ferrand, France

### Contacts:

Séverin Dronet [severin.dronet@michelin.com](mailto:severin.dronet@michelin.com)

Nicolas Malicki [nicolas.malicki@michelin.com](mailto:nicolas.malicki@michelin.com)

Juan Colmenero de Leon [juan.colmenero@ehu.eus](mailto:juan.colmenero@ehu.eus)

Angel Alegria [angel.alegria@ehu.eus](mailto:angel.alegria@ehu.eus)

### Subject :

To maintain its leadership in the tire business, MICHELIN is dedicating a great amount of resources to understand the physical and chemical mechanisms that drive the industrial performance and the quality of its products under various usage conditions. A tire is a composite that integrates a large variety of materials: textiles, metallic cables, elastomers, mineral fillers etc.). Mastering mixing of an elastomer with a higher---T<sub>g</sub> oligomer is a promising route that is currently being explored in order to optimize the dynamical behavior of the final system in relationship with the traction versus rolling resistance compromise needed for tire applications. It is noteworthy that such material belongs to the more general kind of systems categorized as binary mixtures with dynamic asymmetry.

To this kind of materials belong mixtures of components of any nature (polymers, oligomers, nanoparticles, low molecular weight glass-forming systems, ...) which display very different mobility (and thereby, very different values of the glass-transition temperatures) in their neat states. A great deal of effort has been devoted from both, an experimental and a theoretical point of view, to characterize and understand the effect of blending on the dynamics of these systems, in particular on the  $\alpha$ -relaxation [1]. The outcome of the experimental investigations can be summarized in two main observations: (i) the dynamic heterogeneity –presence of two distinct characteristic times associated to each of the components, modified by blending with respect to those of the pure components- and (ii) the broadening of the component response with respect to that of the pure material. These two universal features were also found in the mixtures composed by polymeric chains of SBR and an PS-oligomer (the simplified industrial system explored in the previous project). To describe the dynamical behavior of those blends, the concepts developed for 'academic' model binary mixtures were successfully invoked. These key concepts are (i) the self-

concentration, accounting for the enhancement of the local concentration around a given segment on its own component, due to chain connectivity, and (ii) the ubiquitous presence of thermally activated concentration fluctuations. These two ingredients are responsible for the two experimental observations above mentioned, respectively. Taking into account simultaneously both effects, the dielectric response of the mixtures for a broad range of concentrations was well described [2,3]. From that study, the width of the concentration fluctuations as observed by dielectric spectroscopy was deduced. Furthermore, small-angle neutron scattering (SANS) experiments provided direct microscopic insight into the correlation length of the concentration fluctuations of the blends [2,4]. Applying again theoretical schemes developed for model mixtures [5], the size of the relevant region for the dielectric response could be deduced. To do this, the information from the dielectric study about the width of the distribution of concentration fluctuations and the value of the correlation length from SANS was used as input. The obtained characteristic size for dielectric relaxation turned out to be of about 1nm, independently of temperature and composition, and in agreement with the results reported in the literature for blends of polymers showing much larger correlation lengths for concentration fluctuations [5]. Thus, it seems that this value is universal. This finding opens the possibility to predict the broadening of the relaxation of the components in a mixture just knowing a single parameter: the correlation length for concentration fluctuations, which can be determined by small angle scattering techniques.

The PhD project here proposed aims in extending the above described framework for the SBR/PS mixtures to other binary mixtures. In particular, we want to arrive to a predictive modelling of the broadening of the measured magnitudes (calorimetric glass-transition temperatures and dielectric response) starting from the microscopically determined correlation length for concentration fluctuations. In particular, we will explore the role of (i) topology; (ii) molecular mass and (iii) chemical composition of the high-T<sub>g</sub> component on the structural and dynamical properties of the mixture. As systems, we will investigate mixtures of SBR and (i) PS oligomers with different sizes, ranging from styrene to the maximum molecular weight giving rise to thermodynamically miscible blends with SBR and (ii) commercial resins of different kinds.

The methodology will involve applying calorimetry, dielectric spectroscopy and small angle scattering techniques. In order to determine well the correlation length of the concentration fluctuations, we will use materials with deuterated SBR synthesized at Michelin laboratories and apply SANS techniques. Being the other component protonated, this labeling produces a high contrast for neutron scattering. WAXS and SAXS available at the CFM will also be applied for the structural characterization.

- [1] J. Colmenero and A. Arbe, *Soft Matter* 3, 1474 (2007).
- [2] T. Gambino, PhD Thesis.
- [3] T. Gambino et al, 'Modeling the Effect of Concentration on the  $\alpha$ -Relaxation in SBR/PS Blends', in progress.
- [4] T. Gambino et al, 'Relating Concentration Fluctuations as Revealed by Dielectric and by SANS Experiments on a Simplified Industrial System', in progress.
- [5] S. Shenogin, R. Kant, R. H. Colby and S. K. Kumar, *Macromolecules* 40, 5767 (2007).