STRUCTURE AND DYNAMICS OF ELASTOMERIC MATERIALS BY MEANS OF ¹H TIME-DOMAIN NMR: EFFECT OF CROSS-LINKING

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Elastomeric materials are nowadays of central importance in many fields of application, where they need to fulfil specific mechanical requirements. The mechanical properties of an elastomeric material take their origin on the features and topology of the polymer network. In fact fixed chemical cross-links and physical entanglements among polymer chains impose notable restrictions on chain mobility and are at the basis of rubber elasticity [1]. An additional reinforcement effect can be achieved by incorporation in the rubber matrix of different nanoparticles, such as carbon black, carbon nanotubes, nanosilica, and clays [2, 3]. So far extensive research efforts have been addressed to the comprehension of the relationships between the "molecular" and mechanical properties of elastomeric materials, but a full understanding is still lacking. In this frame, NMR spectroscopy can play an important role giving access to many structural and dynamics information on wide spatial and time scales. In this work we applied a combination of different time-domain NMR (TD-NMR) techniques to the study of

In this work we applied a combination of uniferent time-domain fight (1D-fight) techniques to the study of elastomeric materials based on isoprene, butadiene and styrene-butadiene rubbers, with application in the tyre industry. In particular the influence of chemical cross-links on the polymer chain dynamics in a wide spectrum of motion frequencies was investigated, by studying samples obtained using different vulcanization conditions. ¹H Multiple Quantum (MQ) experiments [4] were used for the measurement of the residual ¹H-¹H dipolar interaction: the latter is dependent on the anisotopic character of the fast reorietations of chain segments and, therefore, it is related to the amount and distribution of the topological constraints within the polymer network. Further and complementary information on different regimes of polymer dynamics were also obtained by means of measurements of ¹H spin-spin relaxation times (T₂) and variable temperature ¹H T₁ Fast Field Cycling (FFC) [5] experiments.

References:

[1] S. Schlögl, M. L. Trutschel, W. Chassé, G. Riess, K. Saalwächter Macromolecules 47, 2759-2773, (2014).

[2] R. Scotti, M. D'Arienzo, B. Di Credico, L. Giannini, F. Morazzoni, Silica-Polymer Interface and Mechanical Reinforcement in Rubber Nanocomposites. In Hybrid Organic-Inorganic Interfaces; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, pp. 151-198, (2017).

[3] G. Kraus, Reinforcement of Elastomers; Interscience Publishers: New York, (1965).

[4] K. Saalwächter Prog. Nucl. Mag. Res. Sp. 51, 1-35, (2007).

[5] R. Kimmich, Field-cycling NMR Relaxometry: Instrumentation, Model Theories and Applications; The Royal Society of Chemistry, (2019).