

Understanding the interfacial phenomena involved in the adhesion between elastomers : A solid-state NMR approach

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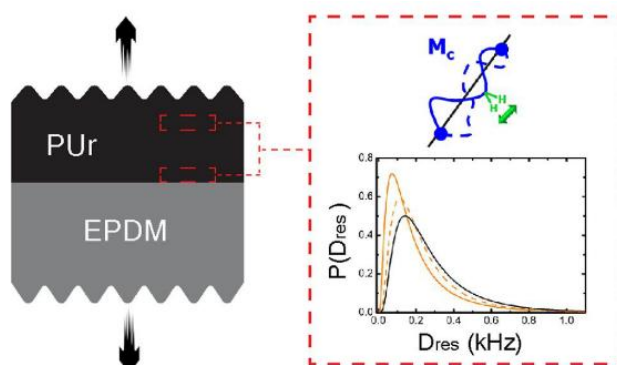
Mots-clés : polyurethane, network topology, interfaces, elastomer bonding, solid-state NMR

Résumé :

Understanding the interfacial phenomena involved in the adhesion between elastomer layers on a molecular basis is an important topic from both fundamental and applied aspects.^{1,2} Nevertheless, this topic has been poorly addressed experimentally. This report aims at rationalizing differences in the adhesion behavior of polyurethane (PU) elastomers cured on an ethylene-propylene-diene terpolymer (EPDM) substrate, based on a detailed description of their local network-like topology, determined thanks to ¹H solid-state nuclear magnetic resonance (NMR) spectroscopy.³

The polyurethanes, composed of the same fraction of hydroxy-terminated poly(butadiene) and isophorone diisocyanate, were cured under different reaction conditions – nature and concentration of the catalyst as well as the crosslinking temperature. The rigid domains formed by the hard segments, the proportion of elastically-active chains and the distribution of the topological constraints in the soft domains were investigated by ¹H solid-state NMR, taking advantage of magic sandwich echoes and double quantum-based experiments. The PU network topology within 20 μm-thick slices collected near the interface with the EPDM layer was systematically compared to the one observed for 60 μm-thick slices, located 500 μm from the interface, corresponding to bulk regions.

Curing at low temperature (30°C) with a low amount of catalyst (0.02 wt %) leads to elastically-active poly(butadiene) chains close to the interface with, on average, higher molecular weights between topological constraints than the ones in the bulk. Such differences between interfacial and bulk regions are not observed any longer as the catalyst concentration is increased to 0.2 wt %. These variations of the local PU network topology, occurring over several tens of micrometers, allow to account for the adhesion testing results.



Distribution of the cross-link density ν ($\propto D_{res}$, the so-called ¹H dipolar coupling) for the PU network at the interface with an EPDM layer and in the bulk region (far from the PU/EPDM interface).

Références :

- [1] : C. Creton; M. Ciccotti, *Reports on Progress in Physics*, 2016, **79**, 046601
- [2] : G. Raos; B. Zappone, *Macromolecules*, 2021, **54**, 10617-10644
- [3] : N. Desgardin; A. Aymonier, C. Lorthioir, *ACS Applied Polymer Materials*, 2023, **5**, 8972-8984