Network Topology of the Interphase between Cross-linked Polyurethane / Ethylene Propylene Diene Terpolymer Elastomers

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Introduction

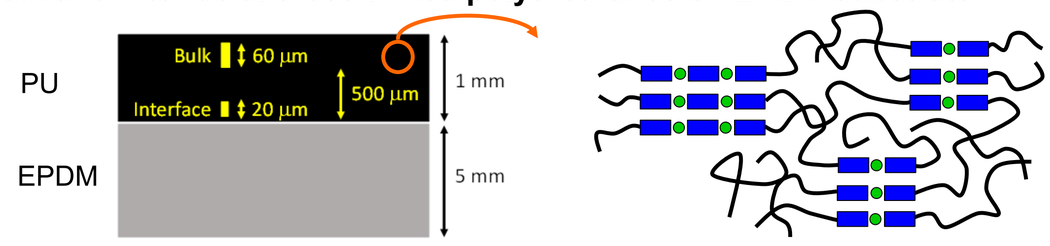
Understanding the interfacial phenomena involved in the adhesion between elastomer layers on a molecular basis is an important topic from both fundamental and applied aspects. Nevertheless, this topic has been poorly addressed experimentally. This report aims at rationalizing differences in the adhesion 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 ^{1}H solid-state nuclear magnetic resonance (NMR) spectroscopy.

Polyurethanes

- Hydroxyl-terminated poly(butadiene)
  M_n = 2900 g.mol^{-1}, I_p = 1.8, functionality = 2.5
- Isophorone diisocyanate
- 2 chain-extender alcohols
- Carbon black (12 wt %)
- Additives (antioxidant, adhesion promoter, and **catalysts**) (< 5 wt %)

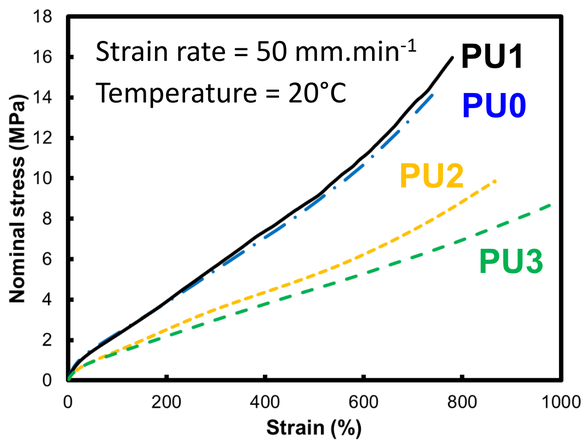
Sample name	Catalyst	Catalyst content (wt %)	Curing temperature (°C)	Duration
PU0	Reference	0.04	65	7 days
PU1	New	0.02	65	7 days
PU2	New	0.02	30	2 months
PU3	New	0.2	30	2 months

Bulk and interfacial cross-linked polyurethanes on EPDM substrate:



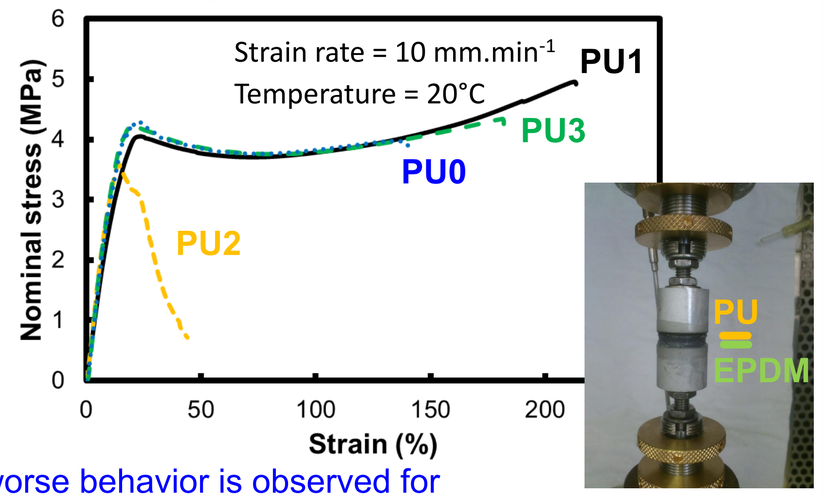
Polyurethanes / EPDM assemblies: Mechanical testing

Tensile tests on PUs:



Similar elastic deformation behavior for PU2 and PU3

Tensile tests on cylindrical EPDM / PU assemblies:

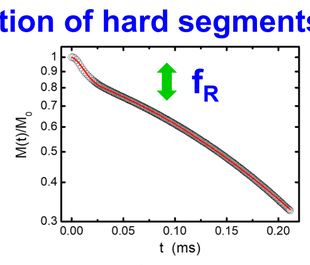


A worse behavior is observed for PU2, as far as the bonding properties are concerned

PU network topology: ^{1}H solid-state NMR

- **Fraction of hard segments f_R:**

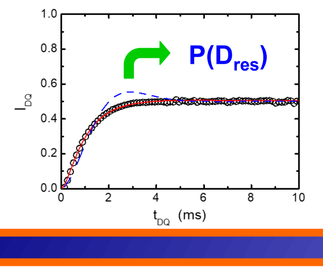
  Bulk PU1

  Magic-Sandwich Echo (MSE) experiments

- **Distribution of the cross-link density G(ν):**

  Bulk PU1

  Double-Quantum (DQ) build-up curves

  ^{1}H dipolar coupling and cross-link density: $D_{res} \propto \nu$

PU network structure in the bulk regions: Influence of the curing conditions

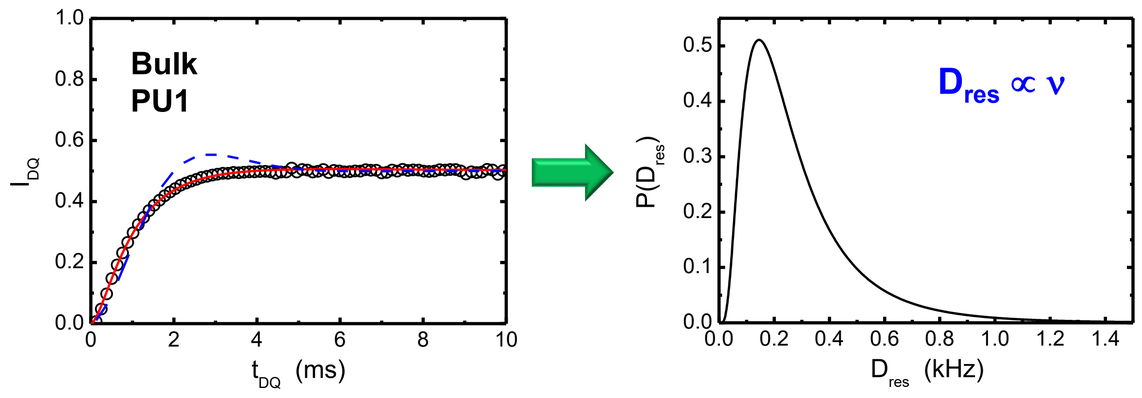
- **Fraction of hard segments f_R:**

Sample name	PU0	PU1	PU2	PU3
f_R (%)	13.1	13.0	12.5	15.5

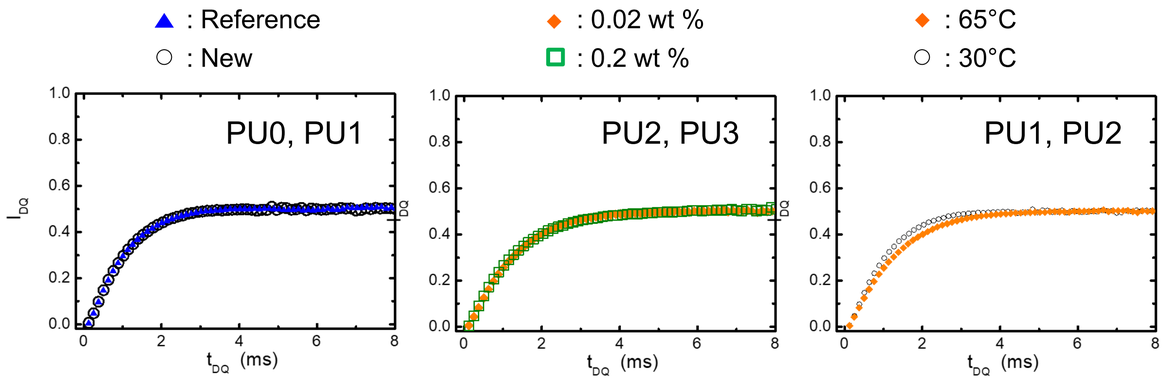
A similar fraction of PU hard segments behavior is formed

- **Topology of the network composed by the soft segments:**

Topological constraints: Chemical cross-links + Hard segments



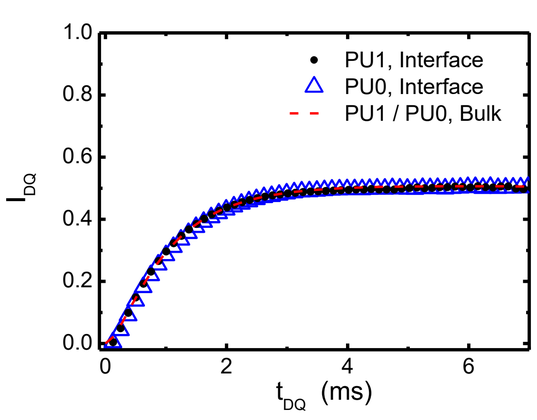
Nature of the catalyst: ▲ Reference, ○ New — Catalyst content: ◆ 0.02 wt %, □ 0.2 wt % — Curing temperature: ◆ 65°C, ○ 30°C



The nature of the catalyst and the catalyst content do not influence the cross-linking of the PB chains

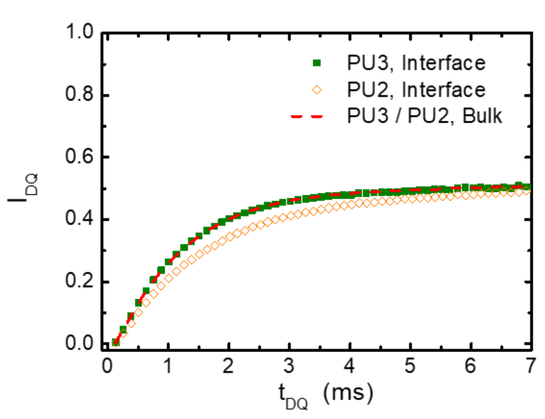
Reduction of the curing temperature → **Network with a lower quantity of longer elastically-active chains**

PU network structure at the interface with the EPDM substrate



Nature of the catalyst

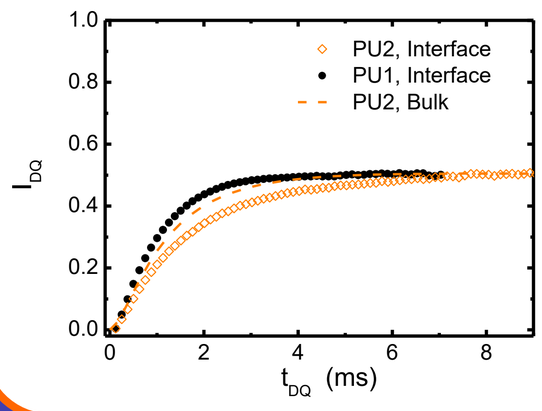
Same network structure in the interfacial regions and in the bulk, irrespective of the nature of the catalyst



Catalyst content

Higher catalyst content

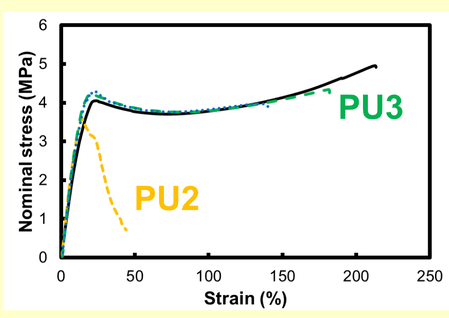
Identical network structure near the interface with EPDM and in the bulk



Curing temperature

The regions close to the EPDM substrate are less cross-linked than the bulk regions

Adhesion behavior



PU / EPDM — Diffusion towards EPDM

c = 0.02 wt %:
Reaction rate << Diffusion rate

c = 0.2 wt %:
Reaction rate >> Diffusion rate

References

[1] Desgardin, N.; Aymonier, A.; Lorthioir, C.; "Network Topology of the Interphase between Cross-Linked Polyurethane/Ethylene Propylene Diene Terpolymer Elastomers for Adhesion Applications", ***ACS Applied Polymer Materials*** (**2023**), 5(11), 8972-8984. https://doi.org/10.1021/acsapm.3c01458.