Nanofillers Modified with Zn Single Sites for Advanced XNBR Composites

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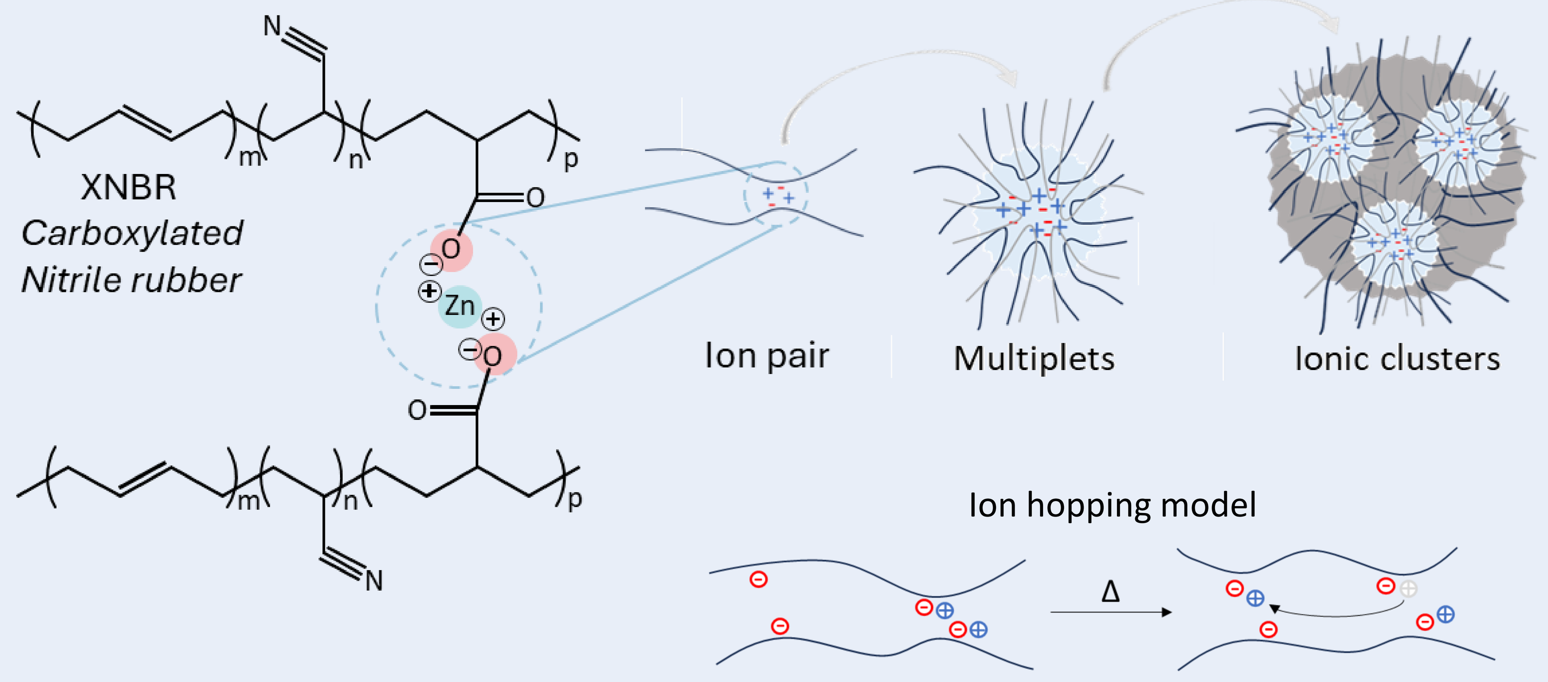
Introduction

The recycling of elastomers remains a critical challenge; a promising strategy to enhance sustainability is the incorporation of **self-healing** properties [1]. **Ionomers** offer a viable compromise by combining the elasticity of rubber with the thermoplastic processability enabled by reversible ionic interactions; this is made by the incorporation of **Zn^{2+} ions** which have been shown to form dynamic bonds with carboxylated nitrile rubber (XNBR) [2]. The present work proposes the design and exploitation of fillers based on Al_2O_3 and sepiolite (Sep) decorated at the surface with Zn(II) single sites [3], both act as **hybrid multifunctional fillers**: they enable self-healing, provide crosslinking, and act as reinforcing agents, while alumina enhances thermal conductivity and sepiolite shows recyclability potential.

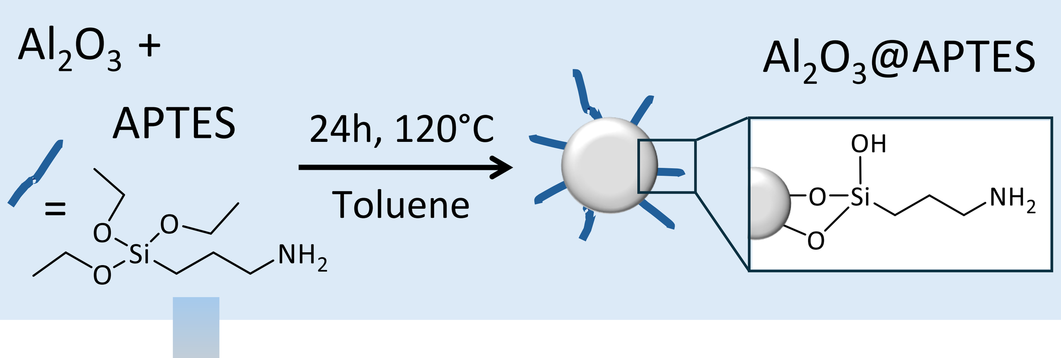


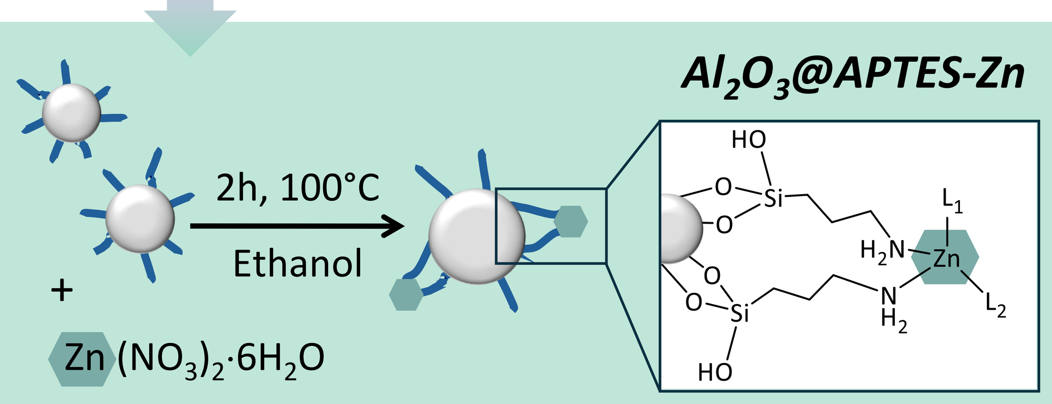
1 Filler Design

to modulate
→ *self-healing*
→ *reinforce properties*
→ *thermal dissipation*

Alumina advantages
- Good thermal conductivity
- Cheap
- Easy to produce
- Available
- Non-toxic
- Electrical insulator

Idea: use a **hybrid multifunctional filler**





APTES functionalization

$$\sigma\left(\frac{n^\circ\ molecules}{nm^2}\right) = \frac{\frac{APTES\ moles\ (mol)}{Al_2O_3\ mass\ (g)} \cdot N_A \left(\frac{n^\circ\ molecules}{mol}\right)}{Al_2O_3\ SSA_{BET}\left(\frac{m^2}{g}\right) \cdot 10^{18}\left(\frac{nm^2}{m^2}\right)}$$

by TGA

σ = 5.70 n° molecules nm^{-2}

by CHNS analysis

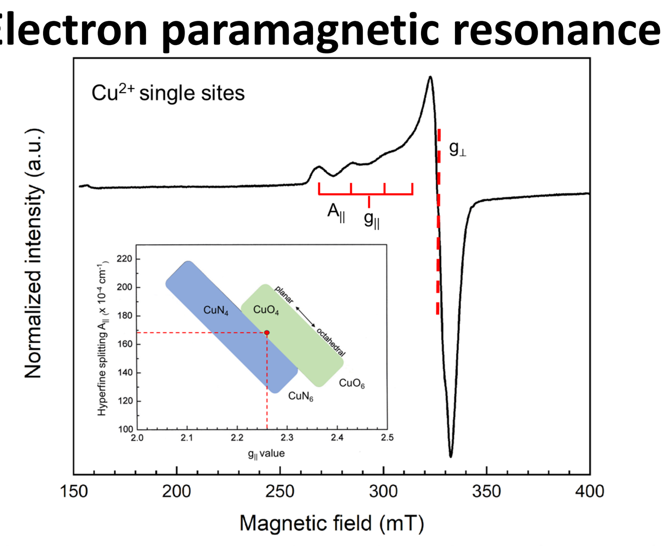
σ(C) = 5.91 n° molecules nm^{-2}
σ(N) = 5.00 n° molecules nm^{-2}

ICP-OES

1.8±0.1 wt. % Zn(II)

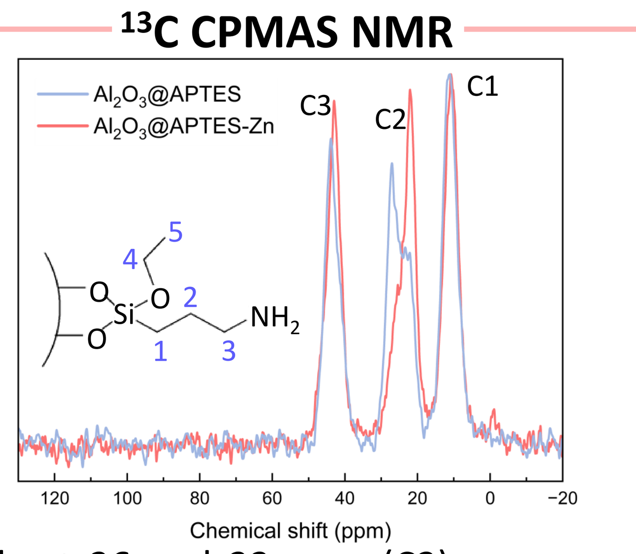
2 Filler Characterization

Electron paramagnetic resonance

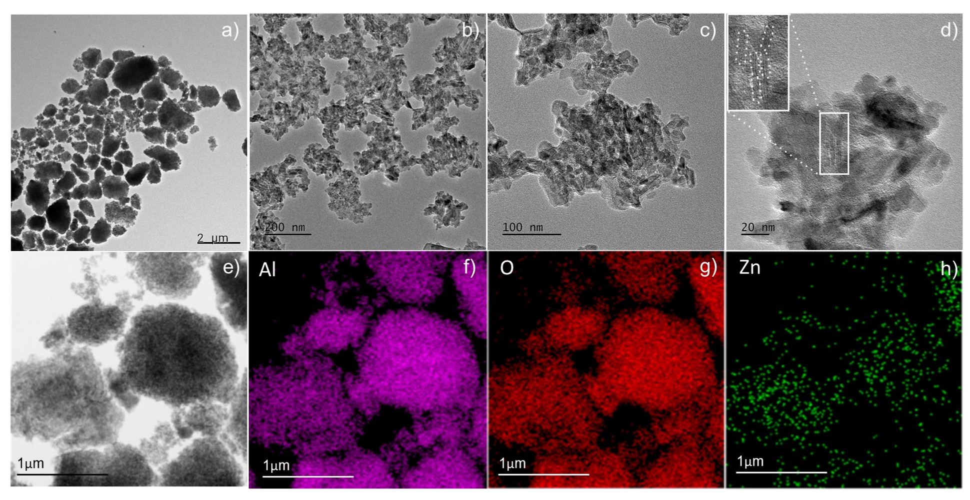


Al_2O_3@APTES-Zn doped with Cu (0.01%)
Tetragonally elongated or square-planar or square-pyramidal complexes bearing two N- and two O-ligands in the equatorial positions.

^{13}C CPMAS NMR



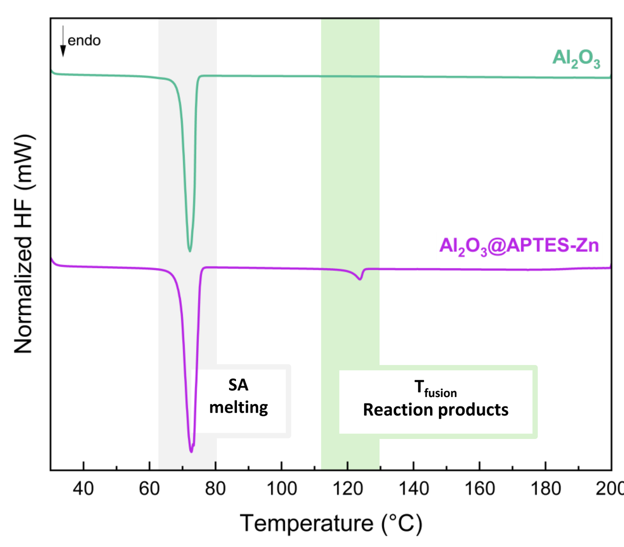
Signals at 26 and 22 ppm (C2) correspond to free $-NH_2$ and interacting amino groups, respectively. Upon Zn loading the free $-NH_2$ signal decreases evidencing Zn interaction.

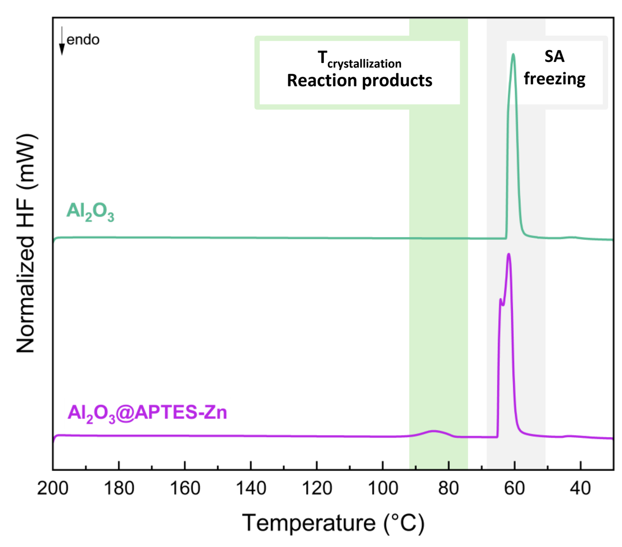


TEM shows micrometric agglomerates constituted by interconnected Al_2O_3 nanoparticles mainly amorphous, with some crystalline planes and **EDX** maps display uniform Zn distribution which are evidence of Zn single sites on Al_2O_3 surface.

3 Study of the Interaction of Filler with SA

Interaction of Al_2O_3@APTES-Zn with Stearic Acid as a **Model Compound Representative of a Simple Carboxylate-Terminated Polymer**: ***DSC analysis*** reveals melting/crystallization transitions of free SA and additional signals due to Zn–SA complexes, confirming effective interactions between Zn centers and carboxylate groups.



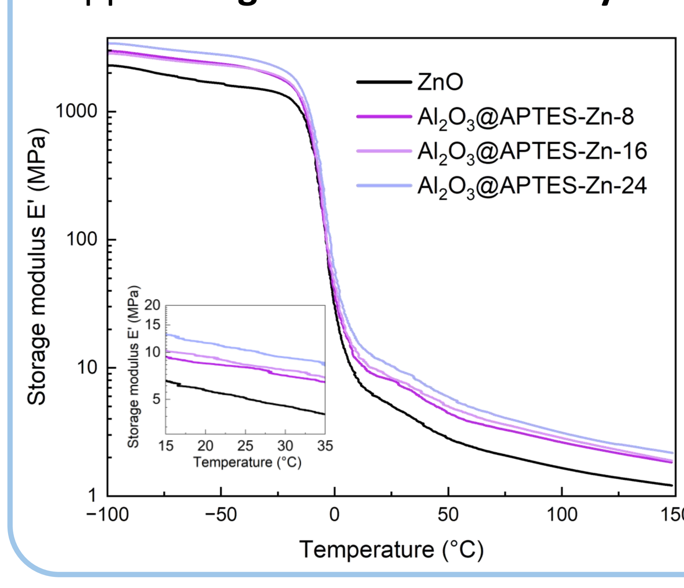


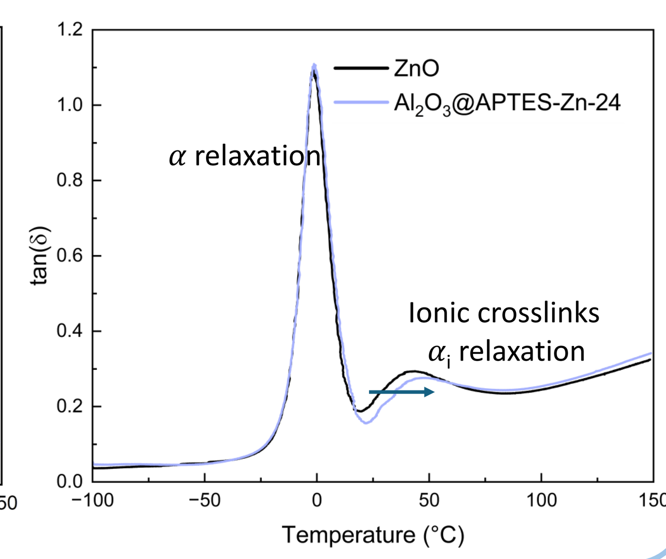
4 Nanocomposite Preparation and Characterization

Filler is included in XNBR, adding ZnO as curing agent, by mechanically mixing and cured by compression molding

Dynamic Mechanical Analysis

Dynamic Mechanical Analysis shows two relaxations: α (Tg ≈ 0 °C) and α_I (**ionic transition** ≈ 50 °C). Increasing Al_2O_3@APTES-Zn loading raises E′ at room temperature, slightly shifts the ionic transition to higher T, and supports **higher crosslink density** via additional ionic cluster sites.

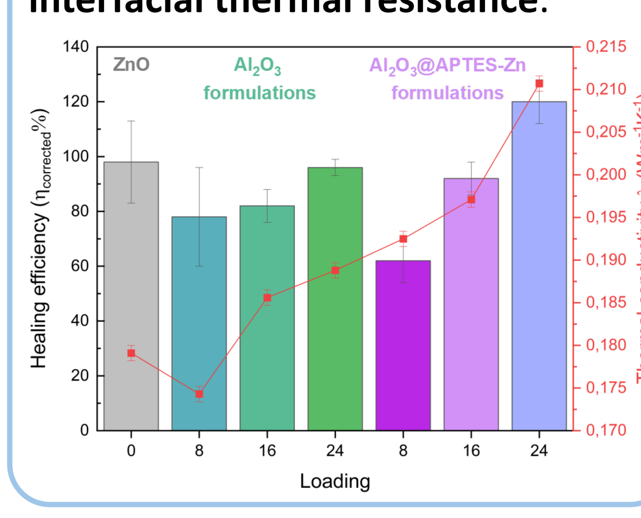




Functional Properties

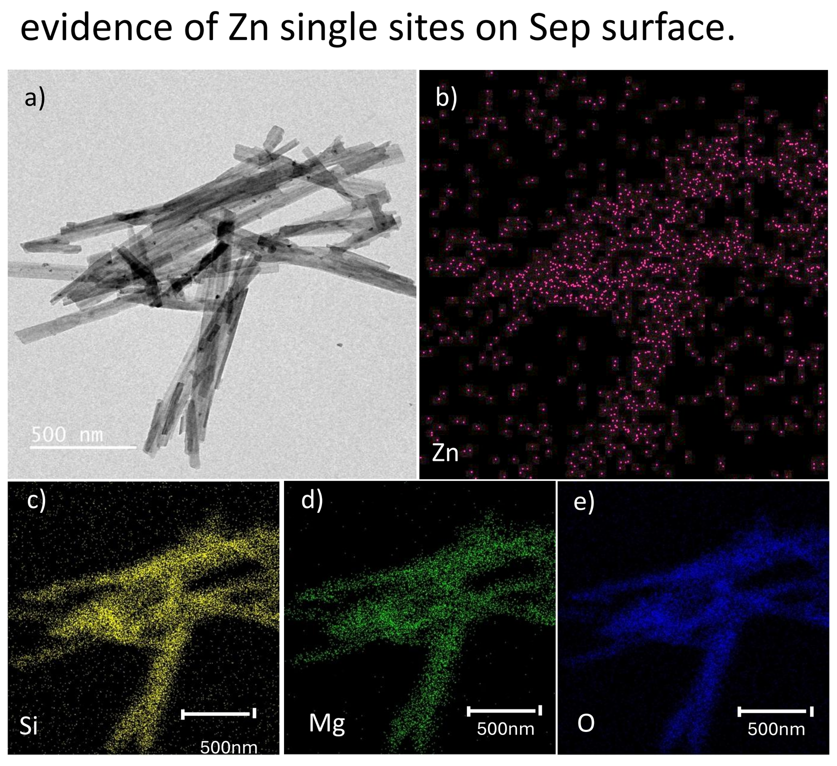
$$\eta(\%) = \frac{TS_{healed}}{TS_{thermal\ treatment}} \times 100$$

Higher filler loading enhances η: Zn centers provide **privileged sites**.
+18% TC due to a reduction of **interfacial thermal resistance.**



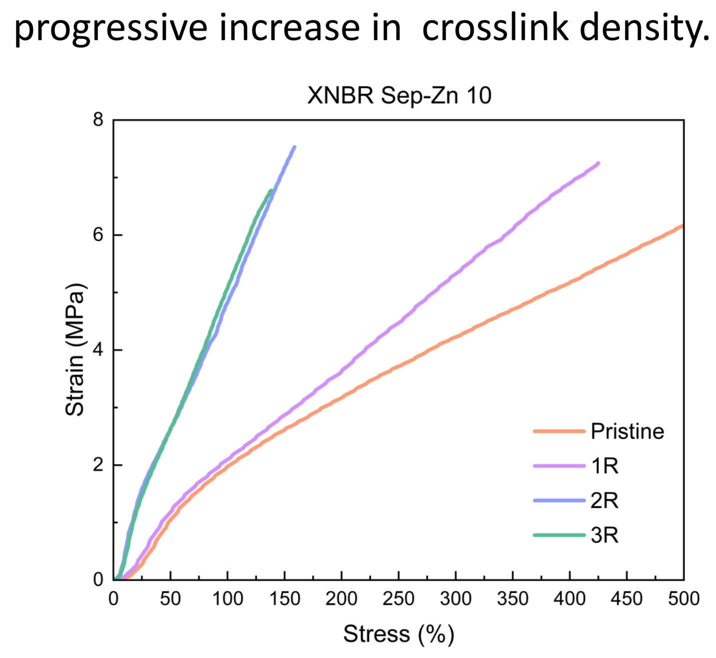
5 Extension of the Approach to Sepiolite Nanofibers

Sep@APTES-Zn *was synthesized via an analogous synthetic route and included in XNBR*
TEM-EDX maps shows uniform Zn distribution, evidence of Zn single sites on Sep surface.

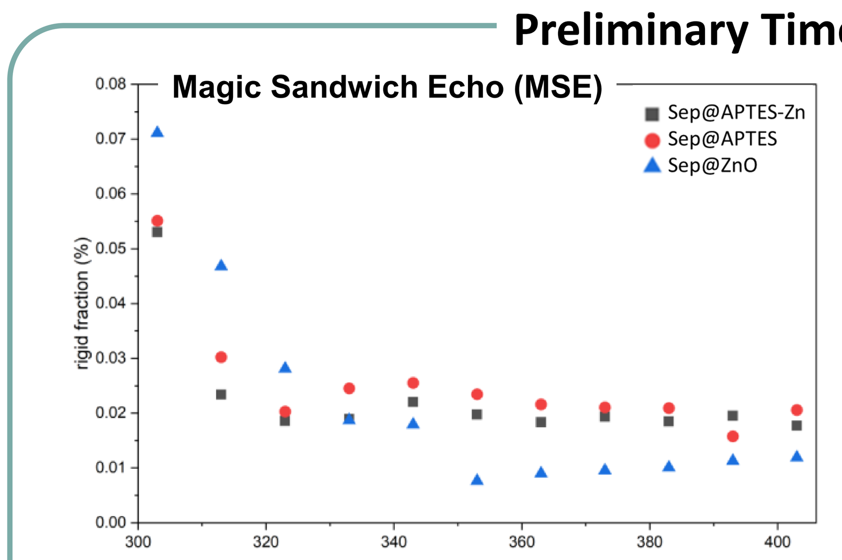


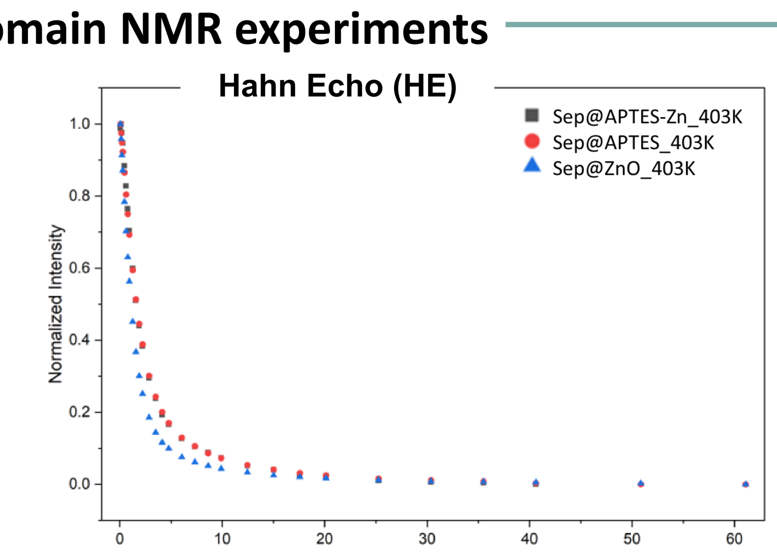
Recyclability

At low deformations (≤300%), compounds show a stiffening effect that becomes more pronounced with recycling, in line with the progressive increase in crosslink density.



Preliminary Time-Domain NMR experiments





The experiments are performed on model formulations made exclusively by filler and XNBR - without any additional curing with ZnO. MSE shows that the **rigid fraction** is generally **low**, even if Sep@ZnO reaches a value of 7% at 300K. Hahn Echo experiments suggest that the presence of ZnO increases the regions with **intermediate crosslinking**.

$$y = A * exp^{\left(-\frac{9}{40}*(D*x)^2\right)} + B * exp^{\left(-\frac{x}{T_{2B}}\right)} + C * exp^{\left(-\frac{x}{T_{2C}}\right)}$$

Sample	B_{Norm}	T_{2B}
Sep@ZnO	0.77052	0.79968
Sep@APTES-Zn	0.58416	0.60235

Conclusion and Perspectives

These results demonstrate a scalable route to mechanically robust, self-repairing, and recyclable ionomeric elastomers, pointing toward greener and longer-life rubber goods. Complementary characterizations (ad-hoc DSC experiment, Time Domain-NMR) highlight the formation of ionic interactions between Zn single sites and the carboxylated groups of the polymer chains, imparting self-healing behaviour.

[1] R. P. Wool, *Soft Matter* **2008**, 4 (3), 400–418; **[2]** S. Utrera-Barrios et al., *Eur. Polym. J.* **2020**, 139, 110032; **[3]** S. Faina et al., *ACS Appl. Polym. Mater.* **2025**, *7*, *1*, 234–246