

Supporting Information

Stress relaxation and thermally adaptable properties in vitrimer-like elastomers from HXNBR rubber with covalent bonds

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FTIR spectroscopy

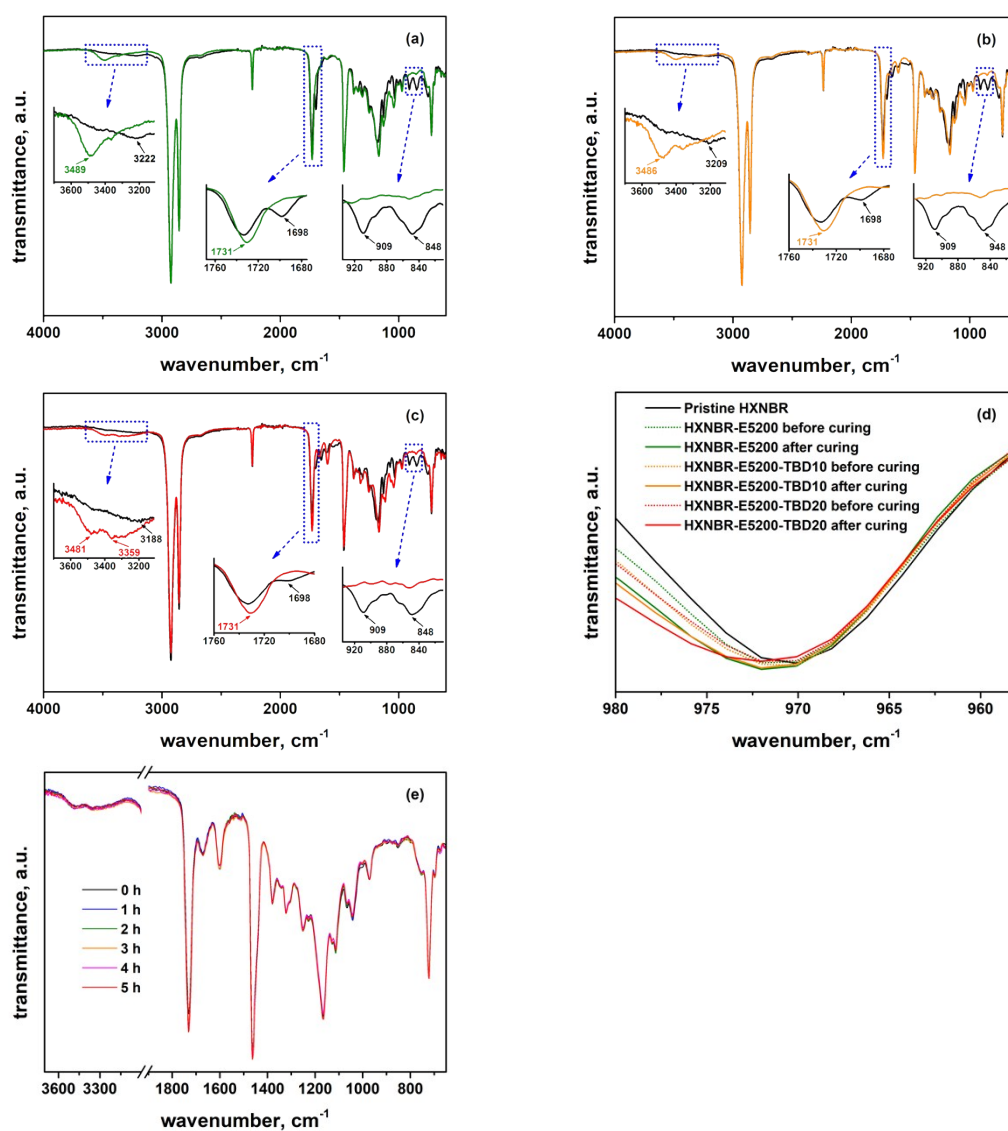


Figure S1 – FTIR spectra of (a) HXNBR-E5200, (b) HXNBR-E5200-TBD10 and (c) HXNBR-E5200-TBD20 before (black curves) and after (coloured curves) curing at 180 °C to the respective t₉₅ values. (d) Comparison of the absorption band at 972 cm⁻¹, corresponding to the vibration of 1,4-trans double bonds in HXNBR, for the three different compounds before and after curing, and the spectrum of the pristine HXNBR. (e) Evolution of the spectrum of a sample of HXNBR-E5200-TBD20 over time for storage at 180 °C at ambient atmosphere.

Tensile testing

Table S1 - Mechanical properties of the different HXNBR compounds obtained from tensile testing

Rubber compound notation	Tensile strength, MPa	Elongation at break, %	Modul, MPa
HXNBR-E5200	3.36	234	2.93
HXNBR-E5200-TBD10	3.51	223	3.60
HXNBR-E5200-TBD20	3.62	229	3.48

Amplitude sweep measurements

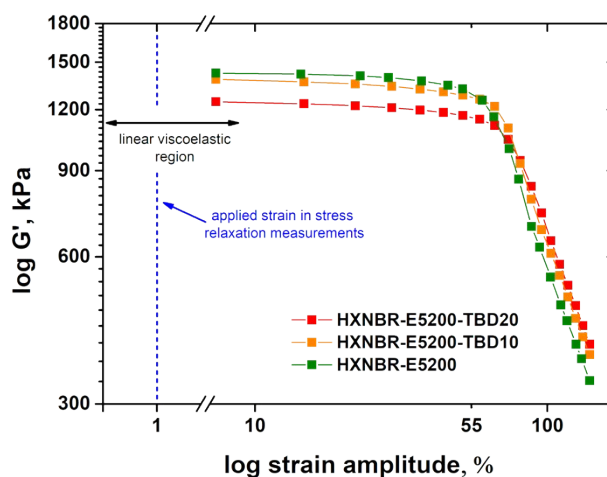


Figure S2 – Amplitude sweep measurements at 180 °C for the different compounds directly after curing up to the respective S' plateau values in the moving die rheometer (green: HXNBR-E5200; orange: HXNBR-E5200-TBD10; red: HXNBR-E5200-TBD20).

Lap shear tests

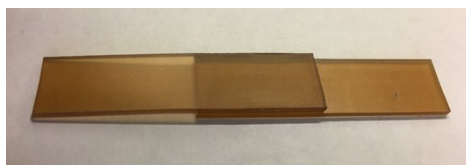


Figure S3 – Photograph of a single-lap joint specimen (an individual strip has a size of 10 × 40 mm) used for lap shear tests to evaluate the HXNBR self-adhesion properties. The overlap length is 20 mm.

Determination of Young's moduli to calculate adhesion energies

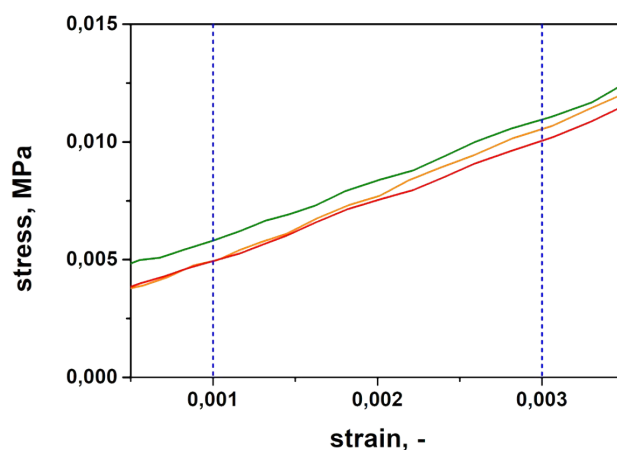


Figure S4 – Stress-strain curves between 0.1 and 0.3% strain of rectangular samples (10 × 40 mm) cut from cured rubber sheets. Tests were performed with a crosshead speed of 100 mm min⁻¹. The Young's moduli were determined as the slope of the respective stress-strain curve between 0.1 and 0.3% elongation.

Experimental setup to investigate the repair capabilities



Figure S5 – Photograph of a typical repaired elastomer sample fixed between two clamps used for stress-rupture tests. To the lower clamp the respective weights with different masses were attached.

Dissolution experiments

Dissolution tests of HXNBR-E5200-TBD20 in trichlorobenzene were performed on rectangular samples with a weight of about 350 mg cut from the cured rubber compound.

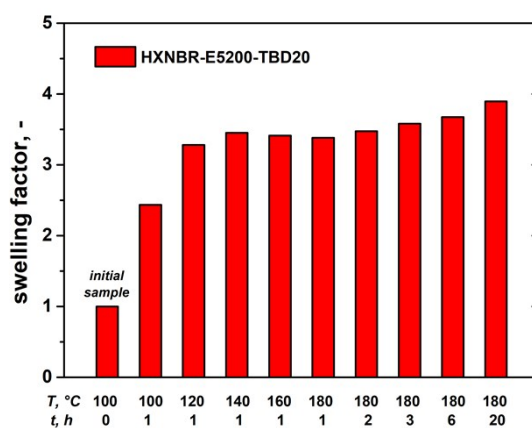


Figure S6 – Swelling data obtained for the immersion of HXNBR-E5200-TBD20 in trichlorobenzene. The temperature was gradually increased from 100 to 180 °C by 20 °C steps and then kept at this temperature for varying times.

Equilibrium swelling experiments

Equilibrium swelling tests in chloroform were performed on rectangular samples with a weight of about 100 mg cut from the cured rubber compounds.

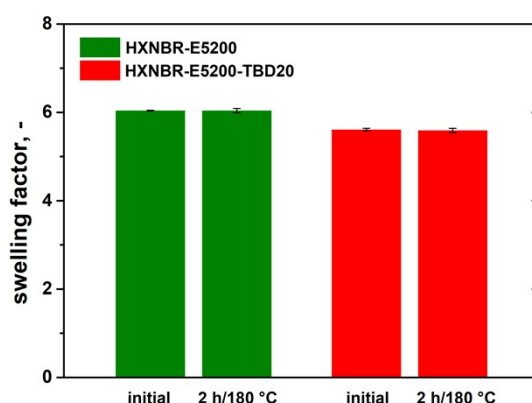


Figure S7 – Equilibrium swelling data obtained for the immersion of HXNBR-E5200 and HXNBR-E5200-TBD20 in chloroform for 48 h. The experiments were conducted with samples before and after storage for 2 h at 180 °C. For each compound and condition, five samples were used and the arithmetic mean value was taken.

Decomposition experiments

Decomposition experiments of HXNBR-E5200-TBD20 were carried out to verify whether the network contains permanent covalent crosslinks besides the exchangeable β -hydroxyl ester linkages. Since the HXNBR rubber under investigation contains about 3.5 mol% residual carbon-carbon double bonds, thermal crosslinking across these bonds could occur. In case that the HXNBR network contains only exchangeable crosslinks, the material should dissolve fully in an excess of ethylene glycol (EG) above the vitrification transition temperature. Since EG is a poor solvent for HXNBR, a 1:1 mixture of EG and trichlorobenzene has been chosen to induce swelling of the sample at the same time and therefore facilitate the incorporation of the alcohol via transesterification exchange reactions. Additionally, triazabicyclodecene was added to accelerate the reaction. For HXNBR-E5200-TBD20, TBD was added in a quantity to obtain a molar ratio of 1:1 with respect to the β -hydroxyl ester linkages. Rectangular samples with a weight of about 150 mg were cut from the cured rubber compound. Figure S8 shows the reaction mixture after stirring for 6 h at 180 °C. The mixture was then poured over a sieve and no gel was found, indicating the absence of permanent, non-reversible crosslinks in the HXNBR.

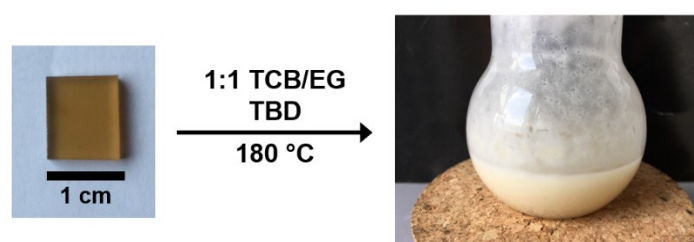


Figure S8 – Photograph of the decomposition experiment of HXNBR-E5200-TBD20 performed in 1:1 ethylene glycol and trichlorobenzene. The photograph shows the reaction mixture after stirring for 6 h at 180 °C.