## Supporting Information

# Design and characterisation of vitrimer-like elastomeric composites from HXNBR rubber

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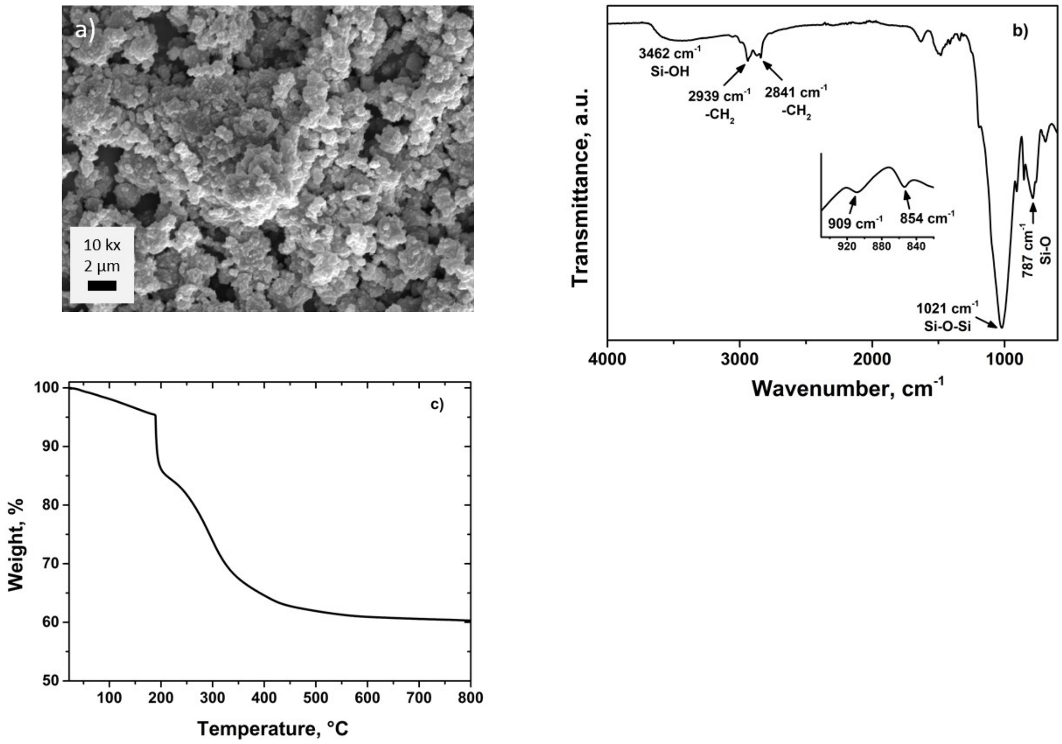


**Figure S1** – Characterisation of epoxy group-functionalised calcium silicate particles: (a) SEM micrograph, (b) ATR-FTIR spectrum, and (c) TGA curve of pristine epoxy group-functionalised calcium silicate particles Rima Sil 1200.

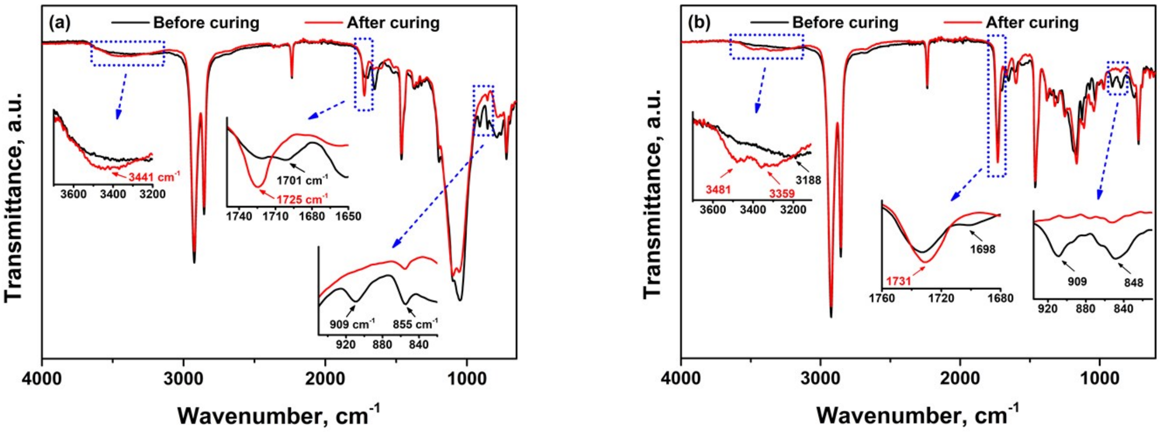


**Figure S2** – ATR-FTIR spectra of (a) HXNBR-Esilicate15-TBD20 and (b) HXNBR-E5200-TBD20 before (black curve) and after (red curve) curing at 180 °C.

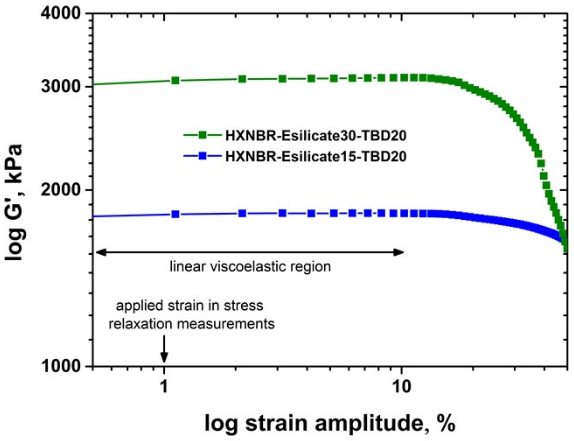


**Figure S3** – Strain sweep measurements of HXNBR-Esilicate composites HXNBR-Esilicate15-TBD20 (blue) and HXNBR-Esilicate30-TBD20 (green). The measurements were performed at 180 °C in the moving die rheometer directly after curing.

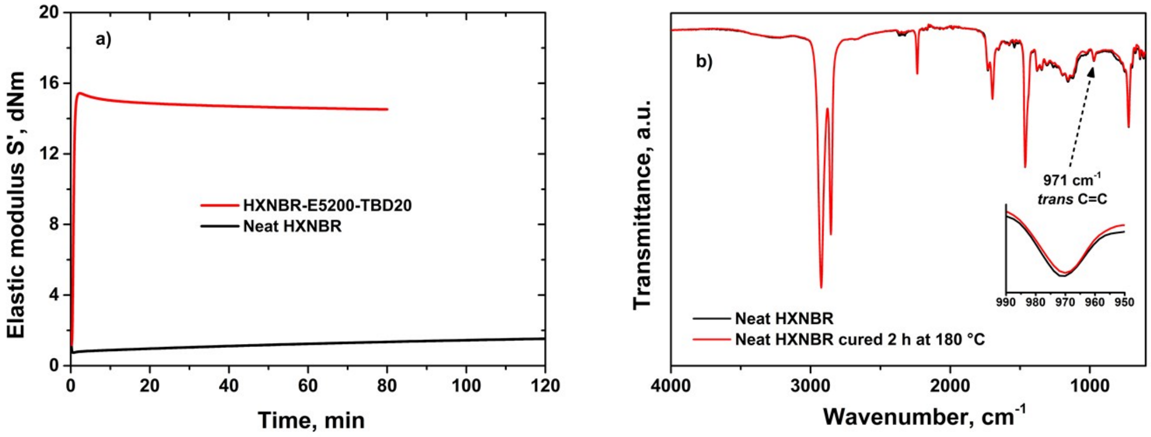
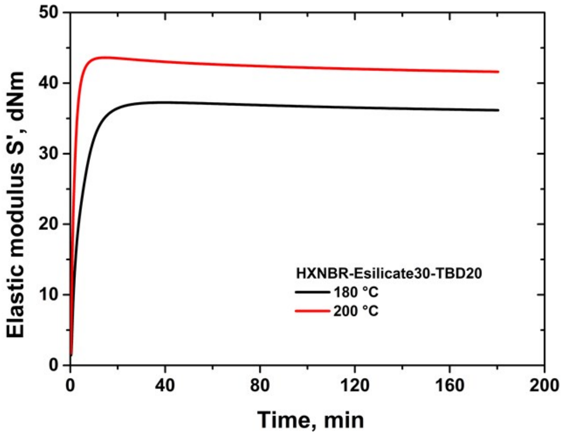


**Figure S4** – The possible formation of permanent covalent bonds due to thermally induced self-crosslinking of the present HXNBR, by either residual carbon-carbon double bonds or the formation of anhydride linkages between two carboxylic acid groups, was examined by rheology and ATR-FTIR spectroscopy. The rheological measurement of neat rubber in the moving die rheometer for 2 h at 180 °C does not indicate the formation of such cross-links. Moreover, ATR-FTIR spectra of neat HXNBR before and after the treatment in the rheometer were recorded. The absorption band at 972 cm$^{-1}$ corresponds to the vibration of 1,4-trans double bonds of the rubber backbone, and no decrease in absorption is observed. The formation of characteristic absorption bands related to anhydrides is also not apparent. Consequently, we assume that no self-crosslinking of the present HXNBR occurs under the conditions applied.

(a) Rheograms of neat HXNBR rubber measured for 2 h at 180 °C in the moving die rheometer and of HXNBR cross-linked with the di-epoxide Epalloy 5200 in the presence of 20 mol% (related to COOH) of TBD (HXNBR-E5200-TBD20).

(b) ATR-FTIR spectra of neat HXNBR rubber before (black) and after (red) the rheological measurement for 2 h at 180 °C in the moving die rheometer.



| HXNBR-Esilicate30-TBD20 | Mass swelling ratio, - | Sol fraction, % |
|---|---|---|
| 3 h at 180 °C | 3.69 | 2.1 |
| 3 h at 200 °C | 3.84 | 1.7 |

**Figure S5** – Left: prolonged rheological measurements of HXNBR-Esilicate30-TBD20 at 180 and 200 °C performed in the moving die rheometer. The rheograms reveal only minor reversion for the composite under investigation even at very high temperatures, whereby the reversion is slightly more pronounced at 200 °C compared to 180 °C. Right: data obtained from swelling experiments (chloroform, 48 h, at room temperature) of the samples from the prolonged rheological measurements. The results show that the *S'* plateau value does not precisely correlate with the mass swelling ratio, i.e. with the density of covalent cross-links. This is probably due to the effect of the different measurement temperatures on the shear modulus, which is typically increasing with temperature in elastomers from rubbers.

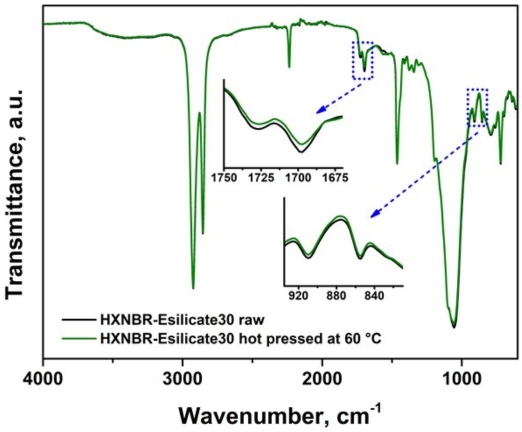
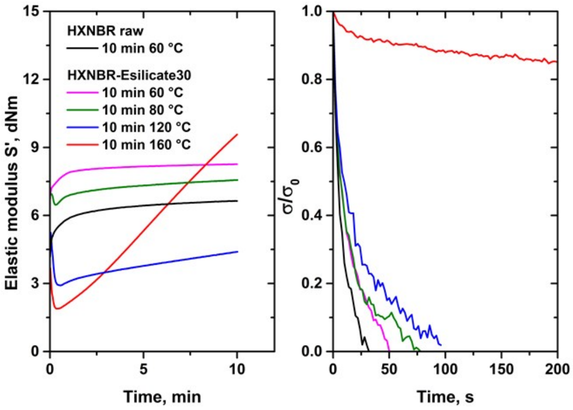


**Figure S6** – ATR-FTIR spectra of a compound from HNXBR containing 30 phr of Esilicate (HXNBR-Esilicate30) before and after treatment in the hot press at 60 °C for 10 min. The spectra are nearly identical, showing only a slight decrease of the absorption bands associated with the epoxy groups on Esilicate (909 and 855 cm$^{-1}$) and with the carboxylic acid groups of HXNBR (1725 and 1701 cm$^{-1}$). These changes may be associated with the formation of few covalent cross-links between HXNBR and Esilicate via the epoxy-carboxyl reaction, which is consistent with the swelling data displayed in Figure S7.

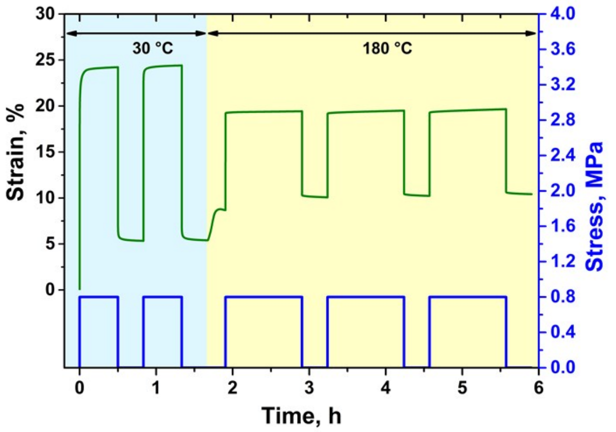


| HXNBR-Esilicate30 | Mass swelling ratio, - | Sol fraction, % |
|---|---|---|
| 10 min/80 °C | 118 | 64 |
| 10 min/120 °C | 57 | 31 |
| 10 min/160 °C | 9.8 | 7.3 |
| HXNBR-Esilicate30 fully cured | 3.7 | 2.9 |

**Figure S7** – Left: rheological measurements of raw HXNBR (black curve) and a composition from HXNBR and 30 phr of Esilicate (HXNBR-Esilicate30) performed in the moving die rheometer for 10 min each. For HXNBR-Esilicate30, a stepwise increase of the measurement temperature was carried out to reveal the onset of significant covalent cross-linking. The data shows that the formation of chemical bonds via the epoxy-carboxyl reaction only accelerates considerably from curing reactions higher than 120 °C.

Center: shear stress relaxation measurements of raw HXNBR (black curve) and HNXBR-Esilicate30 performed directly after the respective curing step in the moving die rheometer. A constant deformation of 1% was applied. From the data, it can be concluded that raw HXNBR undergoes full and extremely fast stress relaxation even at low temperatures, what is to be expected for a rubber without covalent cross-links. Moreover, exposure of the reactive composition HXNBR-Esilicate30 to relatively low temperatures for 10 min still allows for full stress relaxation, as probably only few covalent bonds have been formed yet in these samples. However, the stress relaxation time already significantly increases when raising the temperature from 60 to 120 °C in the previous curing step. After a further increase to 160 °C, the subsequent stress relaxation experiment reveals only minor relaxation capabilities of the sample. This control experiment clearly shows that already small quantities of covalent cross-links between the polymer chains of HXNBR and Esilicate are sufficient to prevent stress relaxation of the composites.

Right: to estimate the number of covalent cross-links formed at the different curing temperatures, additional swelling experiments were carried out (chloroform, 48 h, at room temperature). The data shows the different mass swelling ratios obtained in comparison to the value measured for fully cured HXNBR-Esilicate30. As expected, the mass swelling ratio and the soluble fraction decrease with rising curing temperature. The data confirms that at low temperatures only few covalent cross-links were formed within 10 min of curing, reflected by the very high values for the mass swelling ratios and soluble fractions. Importantly, the sample of HXNBR-Esilicate30 cured for 10 min at 160 °C still exhibits a rather low cross-link density compared to the fully cured compound. Nevertheless, substantial stress relaxation is already prevented.



| HXNBR- | % residual deformation after cycle | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| Esilicate30 | 1.38 | 0.12 | 0.20 |
| Esilicate30-TBD20 | 1.08 | 0.27 | 0.24 |
| | Total creep strain cycles 1-3, % | | |
| Esilicate30 | 0.37 | | |
| Esilicate30-TBD20 | 1.44 | | |

**Figure S8** – Left: cyclic strain-recovery profile of HXNBR-Esilicate30 at 30 and 180 °C. Right: summary of the values for residual strain and total creep strain over three strain-recovery cycles at 180 °C derived from cyclic strain-recovery profiles of HXNBR-Esilicate30 and HXNBR-Esilicate30-TBD20 (Figure 8 in the manuscript).

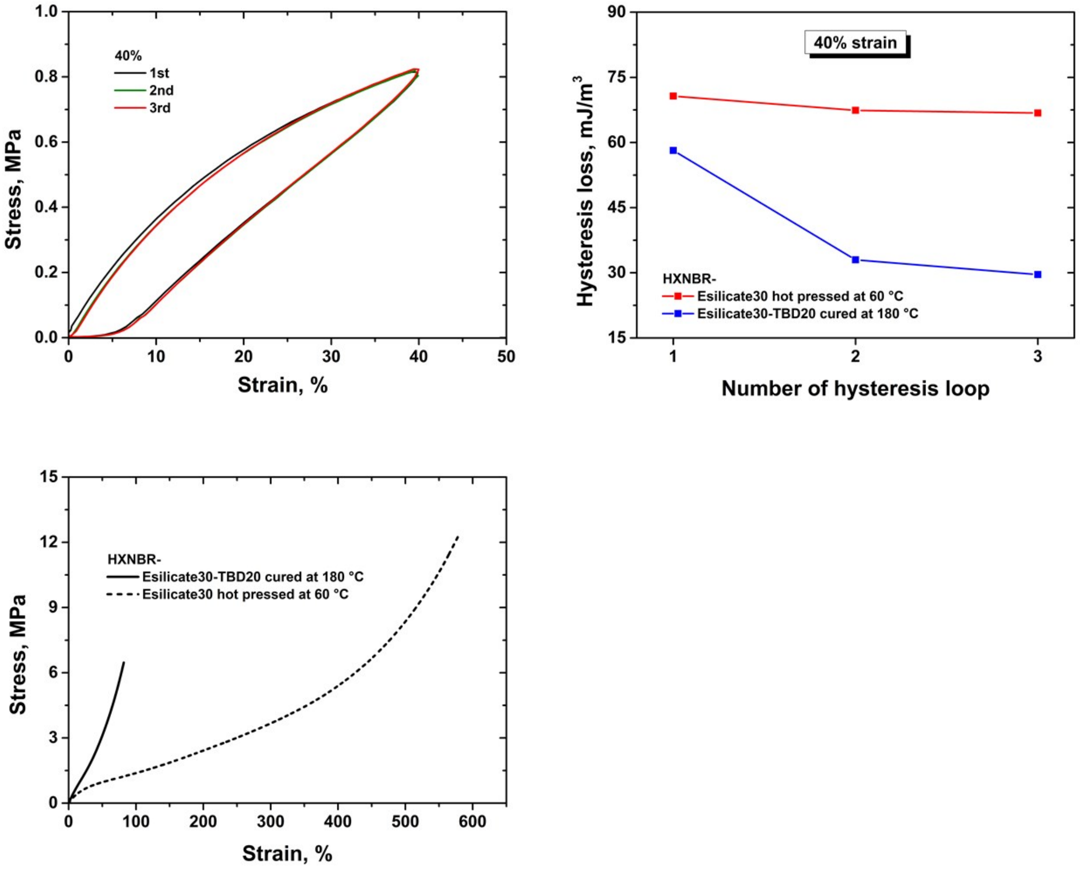


**Figure S9** – Top left: loading-unloading curves of HNXBR containing 30 phr of Esilicate applying a strain of 40%. The composite was hot pressed at 60 °C to avoid the formation of covalent cross-links. Top right: comparison of the calculated hysteresis losses for each hysteresis loop of HXNBR-Esilicate30 that was hot pressed at 60 °C and HXNBR-Esilicate30-TBD20 that was fully cured at 180 °C. The data was derived from the loading-unloading curves at a strain of 40%. Left bottom: comparison of representative stress-strain curves of HXNBR-Esilicate30 hot pressed at 60 °C and HXNBR-Esilicate30-TBD20 fully cured at 180 °C.