Electronic Supplementary Material (ESI) for Soft Matter.

Switching “on” and “off” the adhesion in stimuli-responsive elastomers

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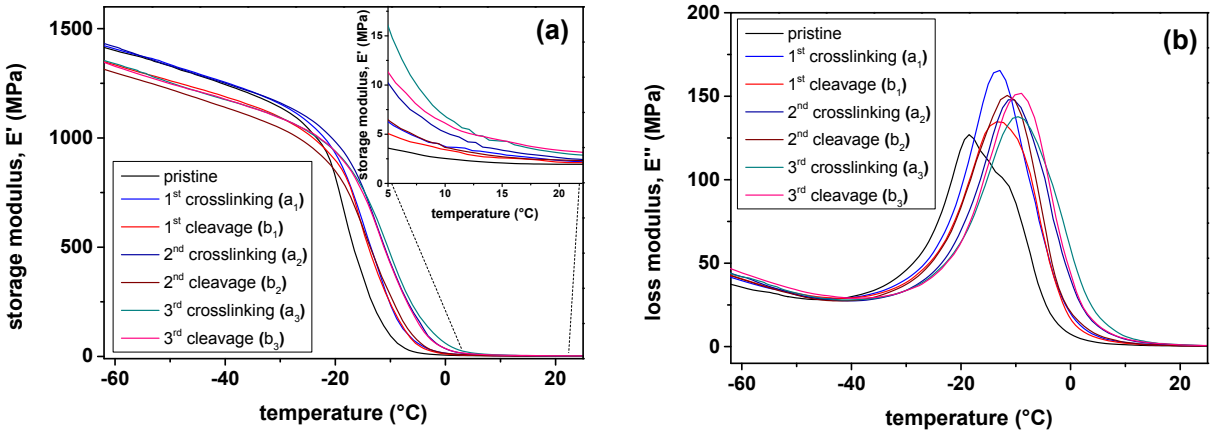
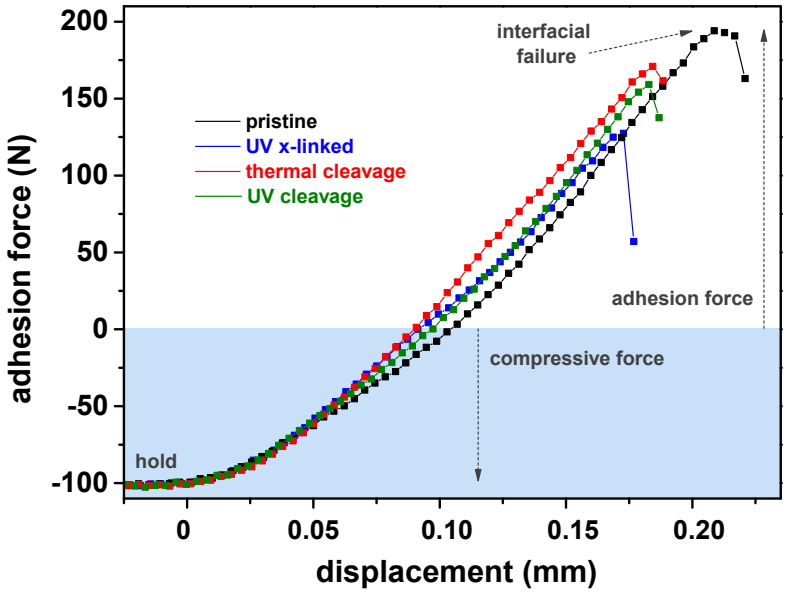
DMA data on anth-HXNBR



Figures S1 – (a) Elastic storage modulus (E’) and (b) loss modulus (E’’) versus temperature of free-standing anth-HXNBR films over repeated cycles of photo-crosslinking (a_1, a_2, a_3) with 46 J/cm² ($\lambda > 300$ nm, N_2) and thermal dissociation (b_1, b_2, b_3) at 70 °C (20 min, N_2).

Load-displacement curves of anth-HXNBR



Figures S2 – Load-displacement curves of probe tack measurements of anth-HXNBR films over one cycle of photo-crosslinking (46 J/cm², $\lambda > 300$ nm, N_2) and subsequent dissociation of the formed photodimers. Dissociation was performed either by thermal annealing at 70 °C (20 min, N_2) or by exposure with deep UV-light (1.1 J/cm², $\lambda = 254$ nm, N_2).

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Background to NMR relaxometry as a tool to quantify reversibility in stimuli-responsive elastomers

NMR relaxometry is a popular technique to study network structure in elastomers. This method is governed by dipolar dephasing brought about by residual dipolar couplings and which is only partially averaged due to non-isotropically fluctuating network segments. The magnitude of D_{res} being directly proportional to non-isotropic nature of motion, which in turn is directly related to the crosslink density (or inverse network chain length, M_C^{-1}) allows a determination of the crosslink density by measuring the corresponding relaxation rates. One of the perquisites for such a study is that T_2 should be measured in conditions where the network segments have completely explored the available conformational space such that the anisotropicity is a function of motional restriction. This is usually achieved by measuring at 50 - 100 K above the glass transition temperature. This is clearly at crossroads for the samples under investigation, since higher temperatures changes the crosslinked state of the system during the course of the experiment due to cleavage reaction of anthracene dimers. Noting this fact, we have intentionally used T_2 relaxometry as a qualitative tool giving no significance to the absolute parameter values and taking only the relative changes in the parameters into account. This is suffice for the purpose of the study and shows excellent correlation with other characterization methods, at the same time being complimentary to it.

The experiments were carried out at 45 °C, which is 50 K above $T_{g.}$ of the elastomers. It is also worth mentioning that no Gaussian shape was seen neither in a simple FID nor a magic-sandwich echo refocused FID, which is an indication of absence of any rigid sub-species at the measured temperature. Relaxometry curves were measured with Hahn echo as a function of echo times. The echo curve were analyzed as mentioned above to arrive at a single parameter (R_2^{avg}). Further, the maximum value of R_2^{avg} during the cycle was normalized to '1' symbolizing the maximum crosslinked state and the minimum to '0' to symbolize be the least crosslinked state, which happened to be the un-crosslinked state. The changes in the overall crosslinked density of the sample is shown for the thermally cleaved sample and UV-cleaved sample. It has be once again pointed out that these values are representative and has no physical significance.

Adhesion force measurement

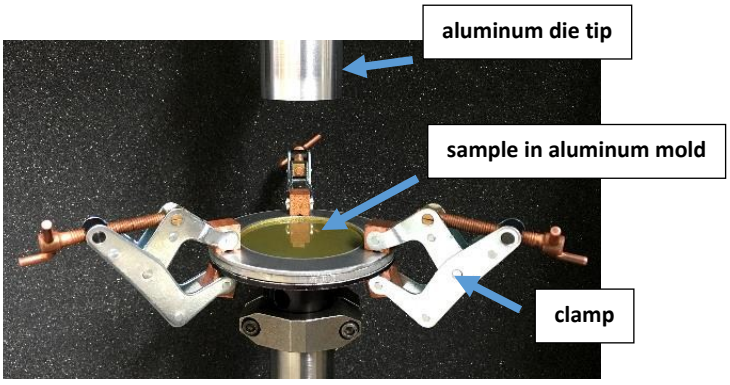

Figure S3 – Experimental set-up for determining the adhesion force of anth-HXNBR films.