Supplementary Information

To account for time-dependent differences between elastic properties measured via macroscale DMA experiments and via torsional harmonic AFM-based indentation, we employed the well known Williams-Landel-Ferry (WLF) theory.[18, 31] This theory is based on the demonstrated equivalency between frequency and temperature in viscoelastic solids, wherein the elastic modulus measured at high frequency can be shifted to a corresponding low frequency value with a master curve. We measured the elastic properties of HNBR at 1 Hz via DMA, over a temperature range from -30°C (T_g) to 25°C. The master curve of log(E) vs. log(f) in Fig. 8a was thus constructed according to established WLF methods.[31, 35] Note that the elastic modulus of HNBR obtained in this master curve at 60 kHz (the nominal resonance frequency of the cantilever) is 189 MPa, which compares well with that measured via AFM torsional harmonic AFM ($E_{\text{AFM measured}}$ = 170 +/- 39 MPa).

More precisely, the frequency from this master curve that corresponds exactly to the average elastic modulus of the HNBR matrix is f = 50 kHz. We can thus establish the shift factor b between these high and low frequency regimes, using $E_{\text{AFM measured}}$ = 170 MPa as the reference value at 50 kHz, and $E_{\text{DMA measured}}$ = 3 MPa as the reference value at 1 Hz, to obtain b = log(50 kHz) – log(1 Hz) = 4.7.

Now, let us consider the elastic modulus of the bound rubber measured by torsional harmonic AFM-based indentation (881 +/- 151 MPa). To obtain the effective stiffness at 1 Hz, we use the above WLF master curve and the shift factor of 4.7. This approach makes the reasonable assumption that bound rubber follows the same curve as the rubber matrix, but is shifted to higher frequencies. This is justified in that the time/temperature equivalence is related to chain mobility, and this bound rubber comprises macromolecular chains of reduced mobility due to the proximity of and local adsorption to chain mobility (not due to temperature). The AFM-measured E_{BR} of 881 MPa corresponds to a higher frequency of 316 MHz on this master curve at room temperature (log (f = 316 MHz) = 8.5). Thus, in this work, at the loading frequency and temperature employed for torsional harmonic AFM, the bound rubber is almost in the glassy state (i.e., approaching a plateau region in the master curve of Fig. 8a). Employing the shift

factor of 4.7 to these AFM-measured E_{BR} data (defined as points within 20 nm of the carbon black perimeter), we calculated that E_{BR} = 53 +/- 11 MPa at 1 Hz and room temperature. Thus, under those conditions, the bound rubber is in a transition between the rubbery and glassy states.