Supplementary Information

Real-space observation of the temporal evolution of nanoscale mechanical heterogeneities in deeply aged polymer glasses

Hung K. Nguyen[1*], Atsuomi Shundo[2,3], Satoru Yamamoto[3], Keiji Tanaka[2,3*] and Ken Nakajima[1*]

[1]Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Institute of Science Tokyo, Tokyo 152-8552, Japan

[2]Department of Applied Chemistry, Kyushu University, Fukuoka 819-0395, Japan

[3]Center for Polymer Interface and Molecular Adhesion Science, Kyushu University, Fukuoka 819-0395, Japan

Corresponding Authors

* Hung K. Nguyen: email nguyen.h.ffa7@m.isct.ac.jp

* Keiji Tanaka: email k-tanaka@cstf.kyushu-u.ac.jp

* Ken Nakajima: email knakaji@mct.isct.ac.jp

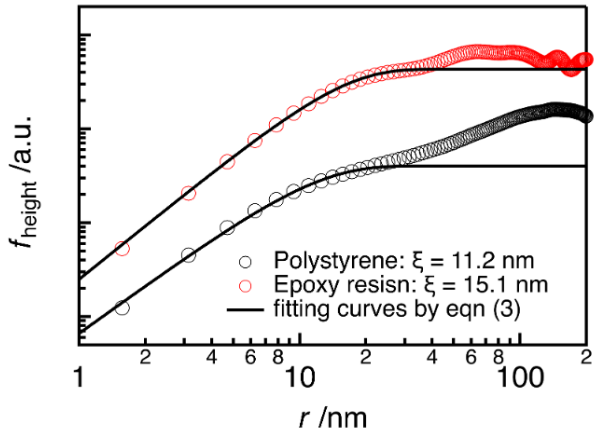


Fig. S1 Correlation functions of AFM topographic images. Correlation functions of nanoscale features derived from the topographic images shown in (**a**) for PS and (**c**) for ERG in Fig. 2 in the main text: solid black curves represent the best fits to experimental data (circles).

Template matching of AFM images using normalized cross-correlation (NCC). Figure S2 shows representative examples of AM-FM AFM topographic and modulus images obtained at $T_a = 303$ K over a period $\Delta t = 2$ h. We can see that the captured images do not cover an identical area due to the thermal drift of the scanning system, but they basically contain a large portion of the same region. To evaluate the evolution of individual HCRs, we focus only on such nearly identical regions, which can be selected using the template matching method via NCC analysis presented in Eq. (4) in the main text.[1] Consider a reference pattern P_0 of size 200×104 pixels highlighted by blue rectangular on the topographic image at $t = 0$, where the height value at each pixel (x, y) is denoted by $H_0(x, y)$. Corresponding region in the modulus image at $t = 0$ is highlighted by white rectangular. After a time interval Δt, the same region is re-imaged, where newly captured pattern corresponding to P_0 is denoted by $P_{\Delta t}$. Due to unavoidable scanner drift, each original pixel (x, y) in P_0 can be relatively shifted to new coordinate ($x-u$, $y-v$) in $P_{\Delta t}$, with the corresponding height value given by $H_{\Delta t}(x-u, y-v)$. $P_{\Delta t}$ is determined matching with P_0 if the NCC index $C(u, v)$ reaches the maximum value (C_{max}). Pattern $P_{\Delta t}$ is obtained by matching topographic images (Fig. S1a), for which C^{H}_{max} is calculated to be 0.97 at $\Delta t = 2$ h, indicating that topographic features undergo almost no change over this time interval. The corresponding C^{E}_{max} for matching modulus images is 0.85 (Fig. S1b), which is relatively smaller than that for the topographic images. This difference can be attributed to the enhanced force sensitivity of the FM mode operated at the higher eigenmode of the cantilever oscillation, which enables the detection of small changes in the elastic modulus that are not accompanied by detectable morphological changes in the AM mode operated at the fundamental eigenmode.[2]

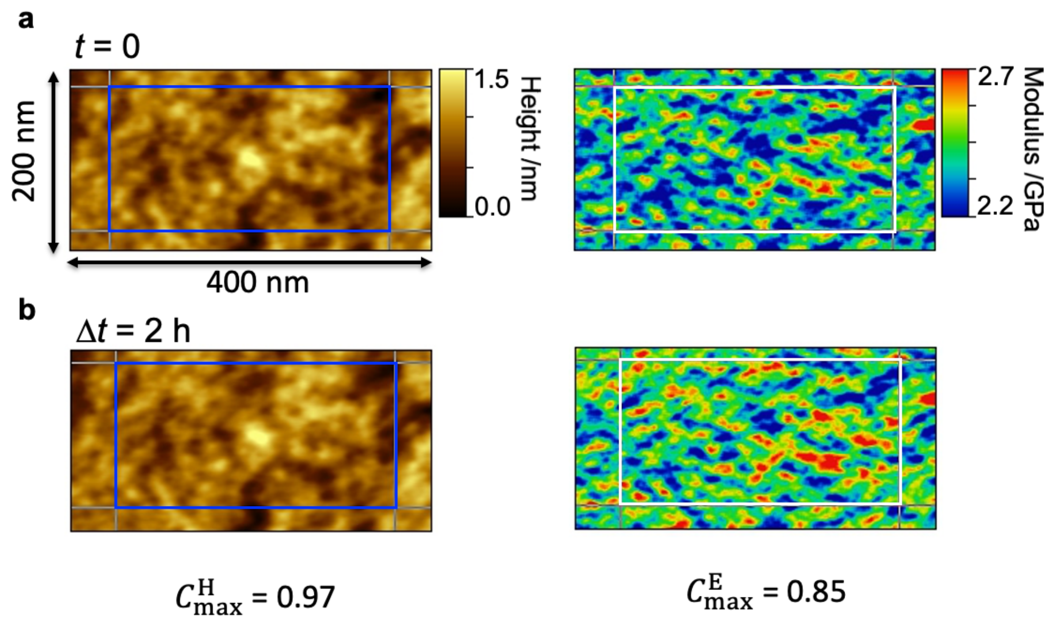


Fig. S2 NCC analysis for template matching of AFM images. a, AM-FM AFM topographic and modulus images of epoxy sample captured at 303 K over an area of 400×200 nm: the time is denoted as $t = 0$ when the scanning starts. **b,** Topographic and modulus images were obtained over the same position after a waiting of 2 h. Regions highlighted by blue (white) rectangular on the topographic (modulus) images represent the selected regions with the highest NCC indexes.

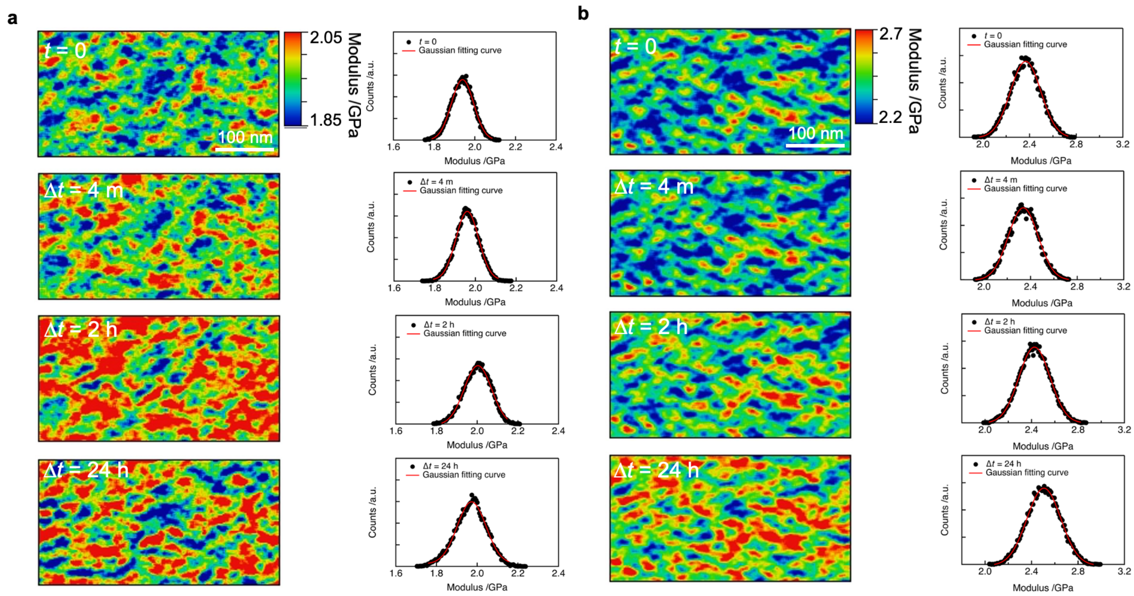


Fig. S3 Original AM-FM AFM modulus images. a, Captured at 358 K over different time intervals with corresponding histograms. **b,** Captured at 303 K over different time intervals with corresponding histograms. Red solid curves represent Gaussian fitting results: the fitted peak values were used to scale the corresponding modulus images.

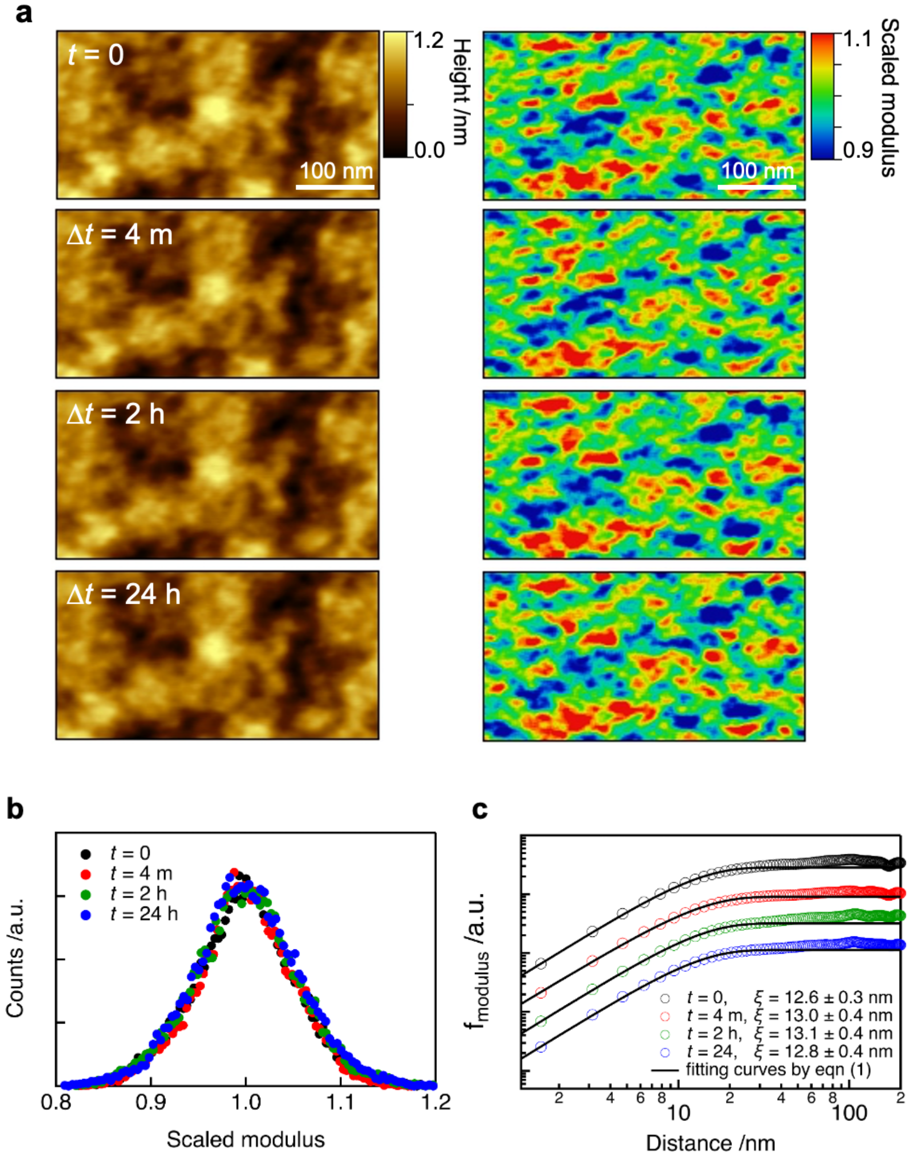


Fig. S4 Evolution of NMHs in ERG during the aging. **a,** AM-FM AFM topographic and scaled modulus images for the sample aged at 323 K over different Δ*t*. **b**, Effect of aging on the modulus distribution. **c**, Effect of aging on the correlation length of NMHs.

Tracking the collective rearrangement of NMHs using NCC index mapping. As discussed in the main text, AM-FM modulus imaging enables visualization of the structural arrangement of NMHs with high spatial resolution. The structural evolution of each heterogeneity manifested by its local mechanical variation can proceed along a specific pathway depending on its intrinsic relaxation dynamics. To visualize the collective nature in the structural rearrangement of NMHs, we simultaneously track the similarity of multiple heterogeneities observed in AFM images acquired at different time intervals. In this analysis, we define a primary unit with a characteristic size ξ, where ξ corresponds to the correlation length of an individual heterogeneity. We first validate this analysis method using two AM-FM images acquired from different surface regions of the epoxy sample at 303 K. Figures S5a and S5b show the corresponding topographic and modulus images, respectively. Since these images are obtained from different regions, no correlation in either topographic or modulus features is expected. The primary unit centered at position (x_0, y_0) is highlighted by a green square in one topographic image, while the blue square in the second image denotes the area used to tract the similarity of the primary unit from the first image. The blue square is chosen to slightly larger than the green square to account for possible small lateral drift between the two images. C_H and C_E, calculated for each primary unit centered at position (x_0, y_0) in topographic and modulus images, respectively, represent the maximum values of the NCC index $C(u, v)$ for the unit. Figures S5c and S5d present the NCC index maps for the topographic and modulus images, respectively. These maps are generated by scanning the (x_0, y_0) position across the entire image, excluding edge regions with a width equal to half the size of the primary unit. The resulting NCC index values are randomly distributed around an average value $<C> = 0$, confirming the absence of correlation between the two images. This analysis procedure is then applied to AM-FM images acquired from the same region of the epoxy sample over different time intervals.

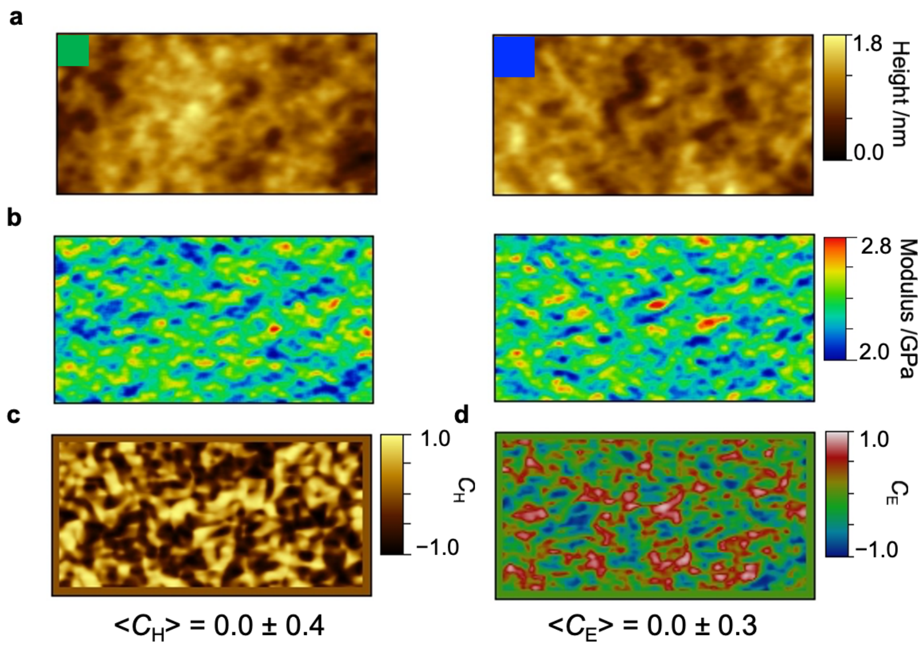


Fig. S5 NCC index mapping of non-correlated AFM images. a,b, AM-FM AFM images captured at 303 K over two different areas for ERG sample **(a)** topographic images and **(b)**

modulus images. **c,d,** Resulting NCC index mappings showing the similarity of NMHs within two **(c)** topographic and **(d)** modulus: the average NCC indices are calculated to be ~0.0 ± 0.4 for topographic images and ~0.0 ± 0.3 for modulus images, confirming the non-correlated behavior between these couple images.

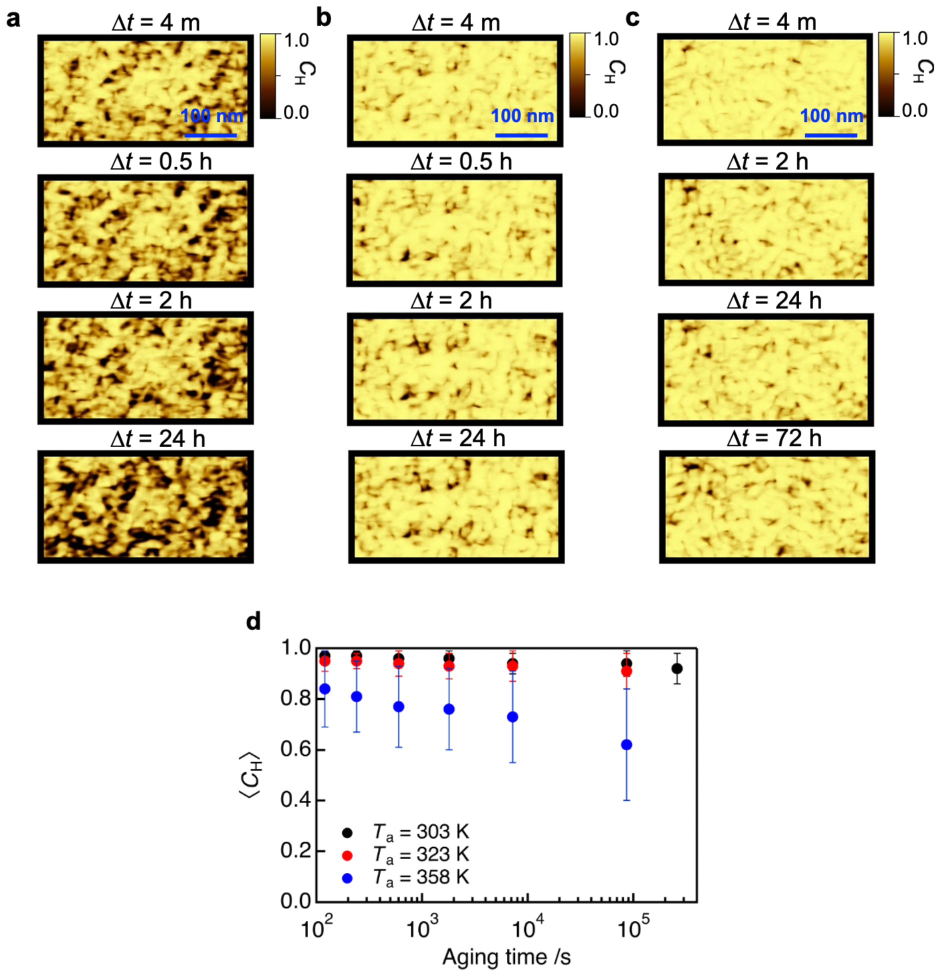


Fig. S6 NCC index mappings obtained for topographic images. a, Aged at 358 K over 24 h. **b,** Aged at 323 K over 24 h. **c,** Aged at 303 K over 72 h. **d,** Average <C_H> values calculated over the entire NCC index mappings as a function of aging time.

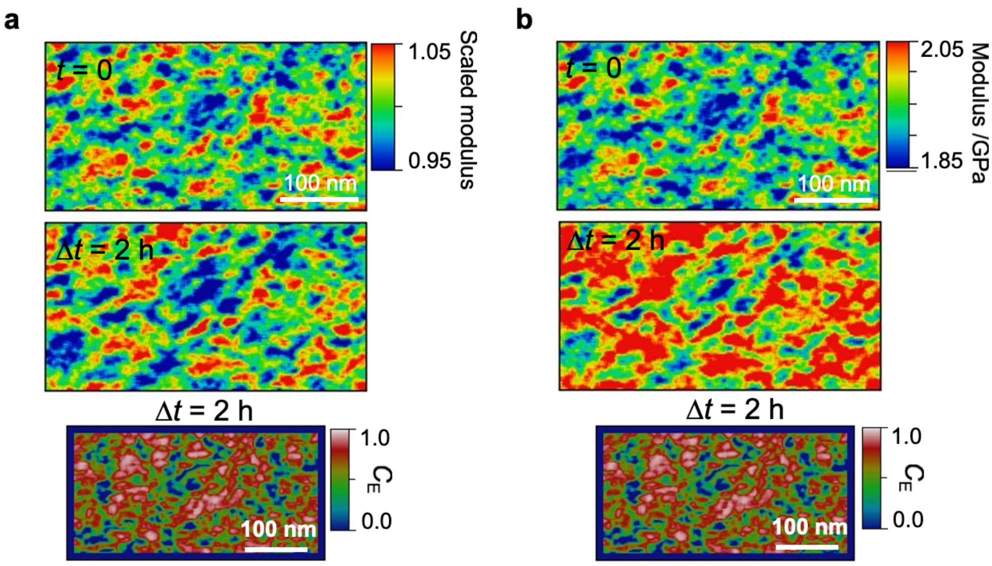
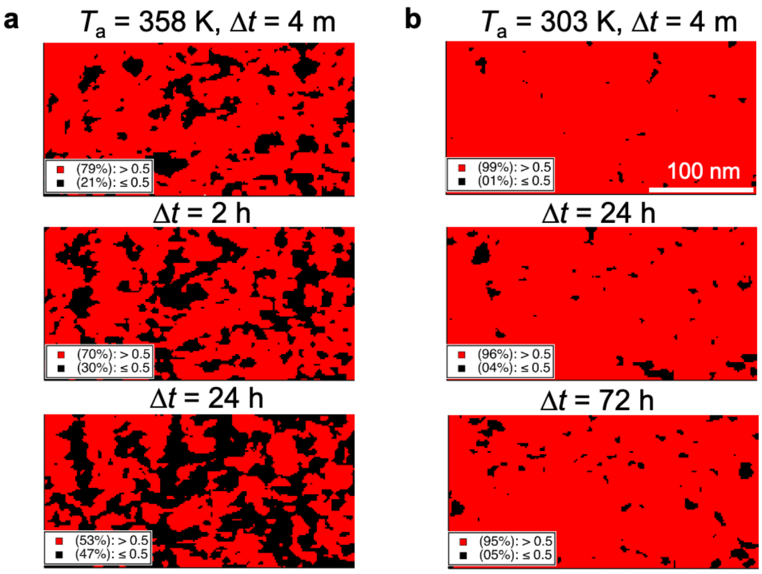


Fig. S7 A comparison of scaling on NCC index mapping. a, Calculated from scaled modulus images aged at 303 K over an interval of 2 h. **b,** Calculated from corresponding original modulus images aged. The obtained NCC index mappings are essentially identical, demonstrating that the scaling has no effect on the resulting NCC index mapping.



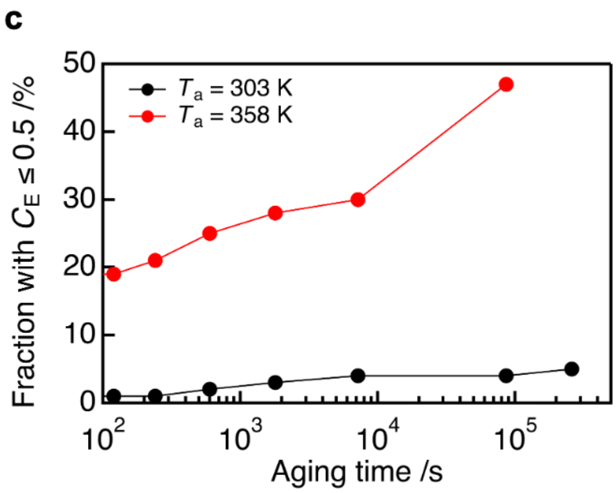


Fig. S8 Fraction of domains with $C_E \leq 0.5$ as a function of aging time. a, Colored maps visualizing domains with $C_E \leq 0.5$ (black) and $C_E > 0.5$ (red) for samples aged at 358 K over 24 h. **b,** Colored maps visualizing domains with $C_E \leq 0.5$ (black) and $C_E > 0.5$ (red) for samples aged at 303 K over 72 h. **c,** Plots of the fraction of domains with $C_E \leq 0.5$ as a function of aging time.

Information on the reproducibility of AFM observations. To prove the reproducibility of our AM-FM AFM observations on epoxy resin samples, we performed AFM measurements across different surface regions of the same ERG sample aged at 303 K as shown in the main text, as well as different ERG samples using different AFM tips. Figure S9a shows topographic and scaled modulus images obtained on a different surface region over a period of 24 h, together with several representative NCC index mappings. Figure S9b shows topographic and scaled modulus images obtained on a different sample over a period of 24 h using a different tip with a calibrated radius of 6 nm, together with several representative NCC index mappings. Figure S9c compares the average value $<C_E>$ calculated by averaging all local C_E values over the entire NCC index mapping, as a function of aging time for different measurements. The results demonstrate the high reproducibility of our AFM observations.

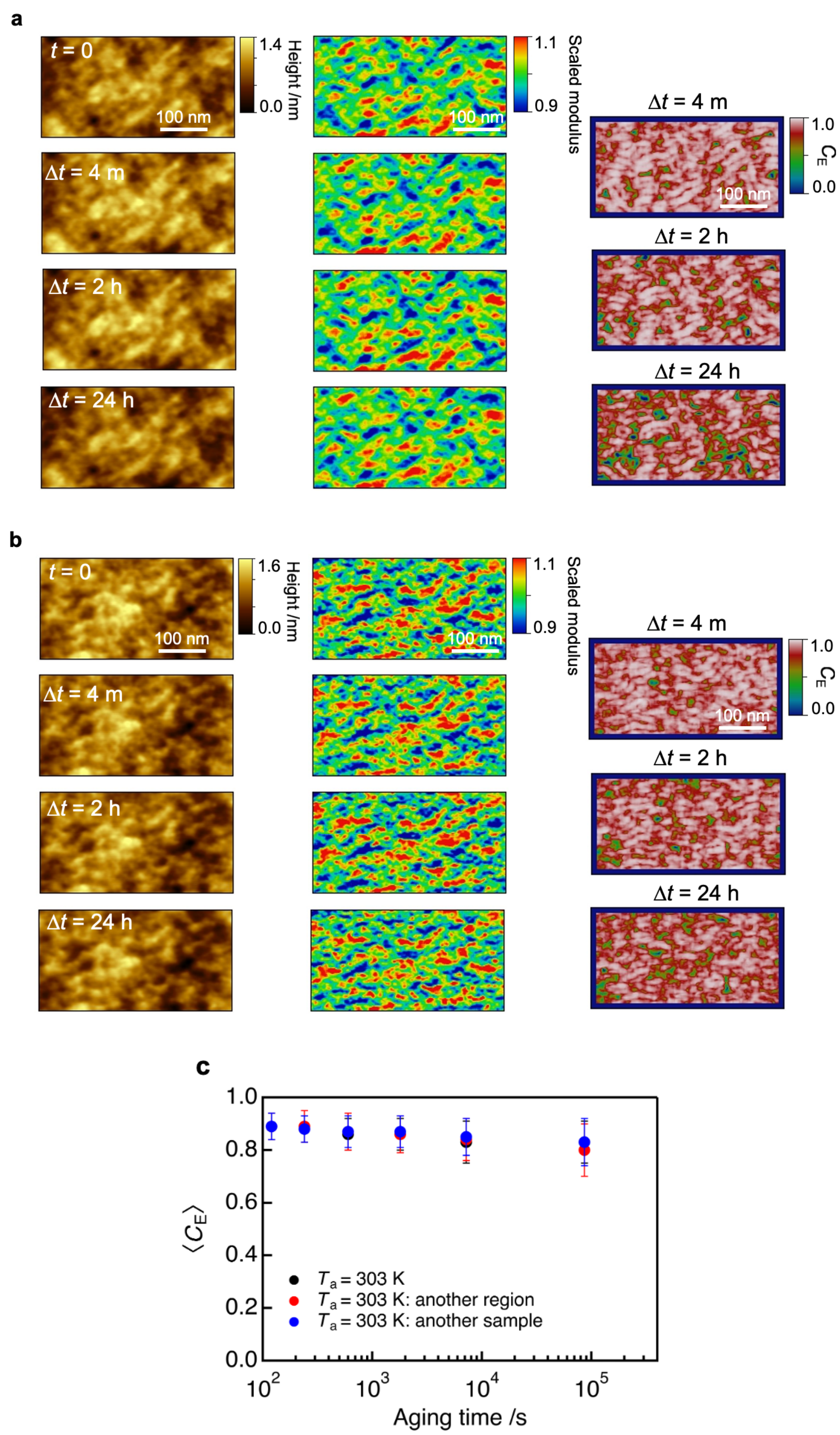


Fig. S9 The reproducibility of AFM observation. a, Topographic and scaled modulus images obtained on a different surface region at 303 K over a period of 24 h, together with several representative corresponding NCC index mappings. **b,** Topographic and scaled modulus images obtained on a different sample at 303 K over a period of 24 h, together with several representative corresponding NCC index mappings. **c,** Plots of the average value <C_E> for different measurements as a function of aging time.

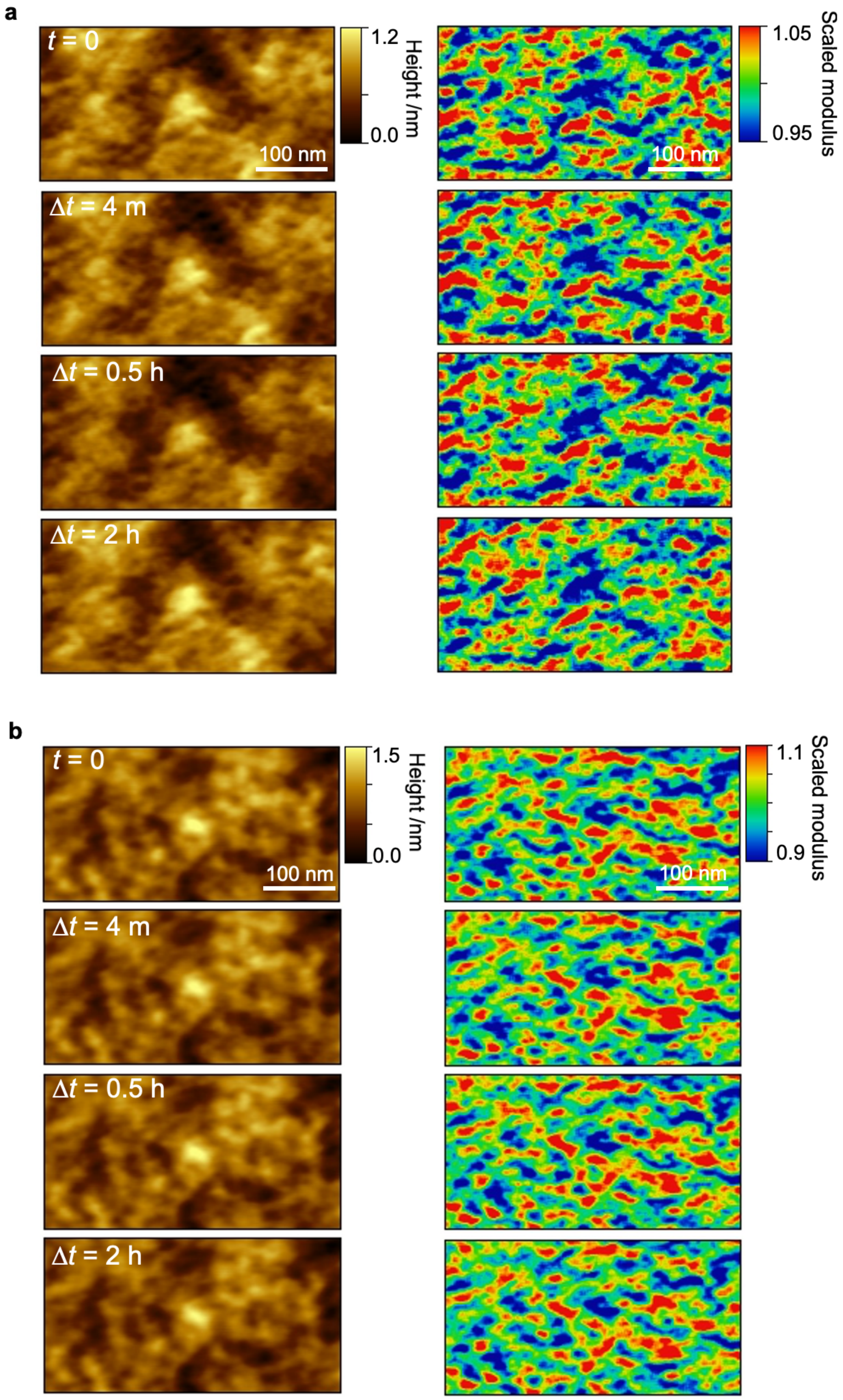


Fig. S10 AM-FM AFM topographic and scaled modulus images of aged ERG. a, After aging at 358 K for 24 h. **b,** After aging at 303 K for 72 h.

1. Tsai, D.-M., Lin, C.-T., Chen, J.-F. The evaluation of normalized cross correlations for defect detection. *Pattern Recognit. Lett.* **24**, 2625–2631 (2003).
2. Lozano, J. R., Garcia, R. Theory of multifrequency atomic force microscopy. *Phys. Rev. Lett.* **100**, 076102 (2008).