nature portfolio

Peer Review File

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

Corresponding Author: Professor Ken Nakajima

This manuscript has been previously reviewed at another journal. This document only contains information relating to versions considered at Communications Materials.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The manuscript reports a very interesting experimental study of the temporal evolution of mechanical heterogeneities in an epoxy resin glass during physical aging at temperatures both near and far below T_g. Using bimodal AM-FM atomic force microscopy the authors show that even 70 K below T_g, where the α-relaxation is expected to be effectively frozen, a subset of nanoscale mechanical heterogeneities undergoes slow and spatially localized rearrangements. This behavior contrasts clearly with the faster and more cooperative evolution observed near T_g. This is an impressive and highly nontrivial experimental achievement, which was obtained by carefully choosing an adequate system. In particular, the work provides what is arguably the first direct real-space evidence that localized rearrangements persist deep in the glassy state, strongly supporting the existence of relaxation mechanisms distinct from conventional cooperative dynamics. The observations are qualitatively consistent with the collective small displacements framework. Overall, I believe this work represents an important contribution to the physics of glassy materials and will be of broad interest to the community working on polymer glasses, aging, and nonequilibrium dynamics. I strongly support publication In Communications Materials after minor revision.

1) The manuscript contains a large number of acronyms and technical quantities, which at times makes the discussion unnecessarily difficult to follow. In particular, figure captions should be written in a more self-contained and descriptive manner, so that the reader can understand the physical meaning of the analysis without constantly returning to the Methods section. As one example, the quantity CE, which is central to Figs. 4 and 5, is never clearly introduced in the main text. The authors should explicitly explain in simple terms what this parameter represents physically, how it is calculated from the modulus maps, and how it differs from the analogous quantity extracted from the topographic images.

2) The statement that ERG results “nicely resemble” those observed in thermoplastic polymer glasses should be softened. In ERG, NMHs originate from inhomogeneous cross-link density generated during curing, whereas heterogeneities in linear thermoplastic polymer glasses have a different structural origin. The possible generalization of the conclusions to other glass-forming systems should therefore be discussed with appropriate caution.

3) The discussion connecting the present observations to previous work on fast aging processes should be clarified and historically better positioned. In the introduction, the manuscript states that the mechanism underlying the faster aging process observed by Cangialosi and co-workers remains elusive, before later relating the present observations to the CSD model. However, recent work (Song et al. Science Adv) has already established a direct connection between the fast equilibration process observed in enthalpy recovery experiments and the slow Arrhenius process (SAP). In particular, Song et al. demonstrated that the process responsible for the fast aging identified by Cangialosi exhibits the same activation barrier and even the same characteristic timescale as the SAP. Within this framework, the CSD model should rather be presented as a microscopic interpretation of the SAP, i.e. as a mechanistic picture proposed to explain its experimental signature.

4) The discussion of the CSD model is appropriate and the present observations appear qualitatively consistent with this framework. The authors could indicate more explicitly that future work could provide a more quantitative connection between

the observed rearrangements and the CSD/SAP framework. In particular, the CSD model predicts a thermal barrier that can in principle be estimated from PVT characterization, while alternatively the same barrier may be extracted experimentally from measurements of the SAP. I fully understand that such an analysis is beyond the scope of the present paper, which already contains a substantial amount of technically demanding measurements, especially considering the exceptionally long experimental times required for these AFM mappings deep in the glassy state. Nevertheless, it would be interesting for future studies to compare quantitatively the timescale of the observed local rearrangements with those expected from SAP/CSD phenomenology.

Reviewer #2

(Remarks to the Author)
Re: Nakajima and co-workers: “Real-space observation of the temporal evolution of nanoscale mechanical heterogeneities in deeply aged polymer glasses"

I read this paper with great interest and recommend publication in Comm. Mat. once the authors have had a chance to reflect on the below minor points. The paper presents a well-performed study of the aging of mechanical heterogeneities performed by means of state-of-the-art bimodal AF microscopy.

1. On p. 2 the authors write that the idea of localized loosely packed regions has “recently been proposed as the microscopic origin…”. This may be, but Johari and Goldstein proposed the same for molecular glasses around 1970! They referred to these regions as “islands of mobility”. A recent extension of this qualitative model, which is not referred to in the paper, however, is that of Gao and co-workers, proposing that percolation is important [Nat. Phys. 21, 471 (2025)].

2. In the discussion the authors refer to a single fast relaxation process (like the Johari-Goldstein distinction between alpha (main) and beta relaxation). If one assumes that there is just one of these extra processes, how does one explain the peak in Fig. 1b that is in-between.

3. In Fig. 2b and 2d I wondered about the scale, but now think it is the same as in Fig. 2a and 2c. I suggest giving this explicitly.

4. Also in relation to Fig. 2, it might be of interest to determine the correlation length also for the topographic mappings (for comparison to that of NMH).

5. I was puzzled about the definition of l and Fig. 2f: Usually a correlation goes to zero at long distances. Why not define the correlation length from Eq. (4)? That would be much more standard. – Incidentally, what is the value of gamma in Eq. (3)? I actually did not understand the definition on p. 17 “the largest lateral distance along…”.

6. On p. 7 the authors write that the local mechanical response becomes increasingly heterogeneous during aging. This refers to a just 10% variation – can we really conclude anything here? If so: Would that be predicted from some model?

7. In line 190 I miss a reference to the glycerol data given.

8. In line 235 is referred to “an apparent percolating network” – is this important?

9. In the discussion, it would be nice if the paper at the end in an outlook contemplates how far equilibration can proceed during long-time aging if only utilizing the beta process? In other words, do the authors expect that the alpha (main) and beta processes work in parallel or in series?

Reviewer #3

(Remarks to the Author)
The manuscript addresses an important and timely problem in glassy materials: the structural origin of faster-than-α relaxation during deep physical aging. The combination of DSC, AM-FM AFM modulus mapping, and NCC-based tracking provides potentially significant real-space evidence for localized rearrangements of nanoscale mechanical heterogeneities. However, the authors should further substantiate the robustness of the AFM/NCC analysis, address possible surface and instrumental artifacts, improve statistical validation, and moderate several overstrong mechanistic claims.

Specific points
1.The manuscript repeatedly states or implies that the observed NMH evolution directly verifies the structural origin of the faster-than-α relaxation process. This conclusion is attractive, but the current data more directly show that local modulus heterogeneities evolve during aging, especially near Tg and, more weakly, deep in the glassy state. The link between these modulus changes and localized configurational rearrangements is plausible, but still interpretive. Likewise, the connection between the AFM-observed local evolution and the DSC-observed enthalpy recovery is correlative rather than fully causal. I suggest that the authors revise statements such as “direct evidence for the structural origin” or “verify the structural origin” to more cautious formulations. This adjustment would make the conclusions better aligned with the strength of the evidence.

2.The central evidence relies on long-duration AM-FM AFM modulus mapping. The authors acknowledge that the average modulus can be affected by small deviations in oscillation parameters, such as free amplitude and phase shift, over long

waiting times, and therefore scale the modulus maps to their peak values before comparison. This treatment is understandable, but it also raises a concern: could the scaling procedure influence the modulus contrast and hence the calculated NCC/CE values? The authors should provide a sensitivity analysis showing that the main conclusions are not dependent on the specific normalization procedure.

3.The AFM measurements are performed on microtomed films transferred onto silicon substrates, whereas the DSC experiments reflect bulk enthalpic recovery. This raises an important question: to what extent do the observed NMH dynamics represent bulk polymer glass aging rather than surface or near-surface relaxation? If available, additional control experiments using different film thicknesses, freshly prepared surfaces, or independently prepared specimens would strengthen the conclusions.

4.The representative AFM images and NCC maps are visually convincing, but the statistical basis of the conclusions is not yet sufficiently clear for a journal such as Communications Materials. The authors should provide more information on reproducibility, including: number of independent samples measured; number of different scanned regions analyzed; whether different AFM probes produced consistent results; error bars for average CE values; distributions of CE values, not only average CE; quantitative fraction of domains with CE < 0.5 as a function of aging time.

5.The DSC results show distinct enthalpy recovery features after aging near Tg and far below Tg, while the AFM observations show different patterns of NMH evolution under corresponding aging conditions. This combination is one of the strengths of the manuscript. However, the connection between these two measurements remains somewhat qualitative. The authors should clarify whether the same aging protocols, thermal histories, and sample conditions were strictly used for DSC and AFM measurements. More importantly, they should explain more carefully how the weak endothermic peak observed after deep aging is quantitatively or mechanistically related to the small fraction of locally evolving NMHs observed by AFM. If possible, the authors could estimate whether the fraction or magnitude of local NMH evolution is consistent with the relative magnitude of the enthalpy recovery signal. Even a semi-quantitative discussion would improve the mechanistic coherence of the manuscript.

6.The manuscript discusses a “faster relaxation process beyond α relaxation.” This is reasonable, but the terminology should be carefully controlled. It would be helpful for the authors to clarify whether they regard this faster process as related to β relaxation, Johari-Goldstein relaxation, collective small displacement processes, or a more general deep-glassy-state equilibration mode.

7.The authors should more carefully justify the use of Hertzian contact mechanics for AM-FM modulus quantification. The epoxy glass is measured not only deep in the glassy state but also at 358 K, close to Tg. Under such near-Tg conditions, the material may exhibit appreciable viscoelasticity, adhesion, dissipation, and time-dependent contact response. Therefore, the AM-FM-derived modulus may be better described as an effective dynamic contact modulus rather than a purely elastic modulus. Since the main conclusion relies on the temporal evolution of local modulus contrast, the authors should discuss how possible deviations from the Hertzian elastic-contact assumption may affect the observed NMH evolution and the NCC analysis.

8.The expression “localized ensembles of loosely packed atoms” is not fully appropriate for the present epoxy polymer glass. This terminology seems to originate from studies of metallic or atomic glasses, whereas the relevant structural units in a cross-linked epoxy network are polymer segments, network strands, or local segmental packing motifs. The authors themselves later discuss the CSD model in terms of segmental movements and local segmental packing, which is more consistent with the polymeric nature of the system. I suggest replacing “loosely packed atoms” with terms such as “loosely packed molecular segments,” “localized segmental ensembles,” or “locally less constrained molecular packing” throughout the manuscript. This would avoid conceptual ambiguity and make the proposed relaxation mechanism more precise.

Several minor comments
1.There are several typographical and wording errors that should be corrected. For example, “NNC” should be “NCC” in several figure captions; “tract” should be “track”; “Nevetherless” should be “Nevertheless”; “species” should likely be “pieces” in the sample preparation section.
2.The manuscript should consistently use either “normalized cross-correlation” or “NCC” after the first definition.
3.The sentence “the evolution of NMHs become much faster” should be revised to “the evolution of NMHs becomes much faster.”
4.The authors should define CE clearly when it first appears in the Results section. Although NCC is introduced in the Methods, the distinction between C, CE, CH, and average CE should be made more transparent for readers.
5.The authors should avoid overusing phrases such as “nicely consistent” and “compelling evidence.” A more neutral scientific tone would improve the manuscript.
6.The phrase “in deep within the glassy state” should be revised to “deep within the glassy state.”

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors modified the text following my remarks. I warmly recommend accepting the manuscript for publication

Reviewer #2

(Remarks to the Author)
I recommend publication.

Reviewer #3

(Remarks to the Author)
The authors have satisfactorily addressed all of my comments and revised the manuscript accordingly. I therefore recommend acceptance of the manuscript.

To reviewer #1:

Thank you very much for taking your time to read through our manuscript and to raise constructive comments, which are very helpful for us to improve our manuscript.

Responses to reviewer's comments:

Comments:

The manuscript reports a very interesting experimental study of the temporal evolution of mechanical heterogeneities in an epoxy resin glass during physical aging at temperatures both near and far below Tg. Using bimodal AM-FM atomic force microscopy the authors show that even 70 K below Tg, where the α-relaxation is expected to be effectively frozen, a subset of nanoscale mechanical heterogeneities undergoes slow and spatially localized rearrangements. This behavior contrasts clearly with the faster and more cooperative evolution observed near Tg. This is an impressive and highly nontrivial experimental achievement, which was obtained by carefully choosing an adequate system. In particular, the work provides what is arguably the first direct real-space evidence that localized rearrangements persist deep in the glassy state, strongly supporting the existence of relaxation mechanisms distinct from conventional cooperative dynamics. The observations are qualitatively consistent with the collective small displacements framework. Overall, I believe this work represents an important contribution to the physics of glassy materials and will be of broad interest to the community working on polymer glasses, aging, and nonequilibrium dynamics. I strongly support publication In Communications Materials after minor revision.

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We added the definition of C_H and C_E into the main text, SI, and Figs. 4 and 5 captions in the revision. In addition, we avoid using several acronyms in all figure captions so that readers can easily understand the discussion. The modification is in red color. See lines 14–17 on page 11, and captions of all figures in the main text.

In our manuscript, C_H and C_E represent the maximum values of the NCC index $C(u, v)$ calculated for all captured nanoscale domains, i.e., the primary unit centered at an arbitrary pixel point (x_0, y_0), with a characteristic length ξ in topographic and scaled modulus mappings, respectively. These mappings are provided in Figs. 3 for epoxy resin glass aged at 358 and 303 K, Fig. S3 for epoxy resin glass aged at 323 K, and Fig. S6 for epoxy resin glasses after aging at 358 K for 24 h and at 303 K for 72.

2. The statement that ERG results "nicely resemble" those observed in thermoplastic polymer glasses should be softened. In ERG, NMHs originate from inhomogeneous cross-link density generated during curing, whereas heterogeneities in linear thermoplastic polymer glasses have a different structural origin. The possible generalization of the conclusions to other glass-forming systems should therefore be discussed with appropriate caution.

We rephrased our statement to avoid the ambiguity in the revision. The modification is in red color. See lines 1–6 on page 4.

We fully agree with the reviewer that the heterogeneous structures present in epoxy resin glasses are fundamentally different from those in thermoplastic polymer glasses and other amorphous materials. Our statement was intended solely to compare the macroscopic mechanical and thermodynamic properties of these systems, as characterized by standard experimental techniques, including dynamic mechanical analysis and differential scanning calorimetry.

3. The discussion connecting the present observations to previous work on fast aging processes should be clarified and historically better positioned. In the introduction, the manuscript states that the mechanism underlying the faster aging process observed by Cangialosi and co-workers remains elusive, before later relating the present observations to the CSD model. However, recent work (Song et al. Science Adv) has already established a direct connection between the fast equilibration process observed in enthalpy recovery experiments and the slow Arrhenius process (SAP). In particular, Song et al. demonstrated that the process responsible for the fast aging identified by Cangialosi exhibits the same activation barrier and even the same characteristic timescale as the SAP. Within this framework, the CSD model should rather be presented as a microscopic interpretation of the SAP, i.e. as a mechanistic picture proposed to explain its experimental signature.

We revised the discussion in the Introduction section to more clearly explain the connection between the earlier work of Cangialosi and co-workers and the recent observations reported by Song and co-workers. The modification is in red color. See lines 17–27 on page 2.

4. The discussion of the CSD model is appropriate and the present observations appear qualitatively consistent with this framework. The authors could indicate more explicitly that future work could provide a more quantitative connection between the observed rearrangements and the CSD/SAP framework. In particular, the CSD model predicts a thermal barrier that can in principle be estimated from PVT characterization, while alternatively the same barrier may be extracted experimentally from measurements of the SAP. I fully understand that such an analysis is beyond the scope of the present paper, which already contains a substantial amount of technically demanding measurements, especially considering the exceptionally long experimental times required for these AFM mappings deep in the glassy state. Nevertheless, it would be interesting for future studies to compare quantitatively the timescale of the observed local rearrangements with those expected from SAP/CSD phenomenology.

We extended the discussion about a quantitative connection between local rearrangements and CSD/SAP framework. The modification is in red color. See lines 11–15 on page 16.

To reviewer #2:

Thank you very much for taking your time to read through our manuscript and to raise constructive comments, which are very helpful for us to improve our manuscript.

Responses to reviewer's comments:

Comments:

I read this paper with great interest and recommend publication in Comm. Mat. once the authors have had a chance to reflect on the below minor points. The paper presents a well-performed study of the aging of mechanical heterogeneities performed by means of state-of-the-art bimodal AF microscopy.

1. On p. 2 the authors write that the idea of localized loosely packed regions has "recently been proposed as the microscopic origin…". This may be, but Johari and Goldstein proposed the same for molecular glasses around 1970! They referred to these regions as "islands of mobility". A recent extension of this qualitative model, which is not referred to in the paper, however, is that of Gao and co-workers, proposing that percolation is important [Nat. Phys. 21, 471 (2025)].

We extended the discussion regarding the possible connection between localized loosely packed regions and fast relaxation process in the revision. We also added the related works reported by Johari and co-workers (J. Chem. Phys. 53, 2372, 1970**) and Gao and co-workers (**Nat. Phys. 21, 471, 2025**) as references 30 and 34, respectively.** The modification is in red color. See lines 2–6 on page 3.

2. In the discussion the authors refer to a single fast relaxation process (like the Johari-Goldstein distinction between alpha (main) and beta relaxation). If one assumes that there is just one of these extra processes, how does one explain the peak in Fig. 1b that is in-between.

We extended the discussion regarding the single fast relaxation process and DSC data in Fig. 1b in the revision. The modification is in red color. See lines 1–6 on page 5.

Our DSC results in Fig. 1 reveal a temperature-dependent shift of the peak position during aging epoxy resin below the T_g, a behavior that has also been observed in other thermoplastic and epoxy glasses (see, for example, in Polymers 13, 954, 2021 and Polym. Eng. Sci. 62, 537, 2022). While such behavior could suggest the presence of multiple fast relaxation processes, it may alternatively be described as a temperature-induced variation in the relaxation dynamics of a single process. The latter interpretation indeed facilitates comparison with several existing theoretical models. Although the difference is relatively subtle, our NNC results in Fig. 4d further suggest that the evolution of NMHs is slightly accelerated at 323 K compared with that at 303 K.

3. In Fig. 2b and 2d I wondered about the scale, but now think it is the same as in Fig. 2a and 2c. I suggest giving this explicitly.

We added scale into Figs. 2b and 2d, Figs. 3a and 3d, in the revision to make it easier for readers to follow.

4. Also in relation to Fig. 2, it might be of interest to determine the correlation length also for the topographic mappings (for comparison to that of NMH).

We calculated correlation lengths for topographic images in Figs. 2a and 2c and presented corresponding plots in Fig. S1 in the SI. We also added the discussion related to these new data in the revision. The modification is in red color. See lines 5–11 on page 7.

5. I was puzzled about the definition of l and Fig. 2f: Usually a correlation goes to zero at long distances. Why not define the correlation length from Eq. (4)? That would be much more standard. – Incidentally, what is the value of gamma in Eq. (3)? I actually did not understand the definition on p. 17 "the largest lateral distance along…".

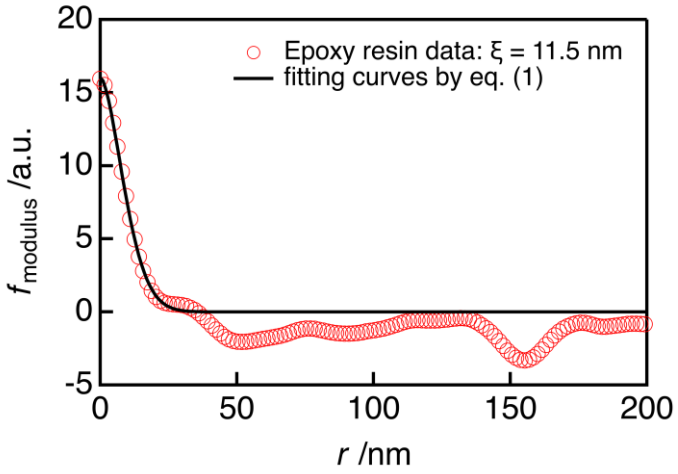
We modified the definition of the correlation length to make it clearer in the revision. The modification is in red color. See lines 14–20 on page 19.

To calculate correlation length of nanoscale features in AFM images, two interchangeable correlation functions are commonly used [*Phys. Rev. B* 48, 14472, 1993]:

$$C(r) = \langle E(r)E(0)\rangle = \sigma^2 \exp[-(r/\xi)^{2\gamma}] \qquad (1)$$

$$F(r) = \langle [E(r) - E(0)]^2\rangle = 2[\sigma^2 - C(r)] = 2\sigma^2\{1 - \exp[-(r/\xi)^{2\gamma}]\} \qquad (2)$$

Relying on eq. (1), the correlation function goes to zero at long distances, whereas it goes to a constant using eq. (2). In principle, we can use both functions for calculation of the correlation length of NMHs observed in modulus images, but here F(r) function is preferred to avoid the presence of negative data (see Figure), which have no physical meaning by fitting.



6. On p. 7 the authors write that the local mechanical response becomes increasingly heterogeneous during aging. This refers to a just 10% variation – can we really conclude anything here? If so: Would that be predicted from some model?

We extended the discussion regarding the change of the size of NMHs during aging in the revision. The modification is in red color. See lines 12–16 on page 9.

Here, our main purpose is to compare the characteristics of NMHs in epoxy resin during aging at different temperatures. In particular, the size of NMHs is found to increase when aging near

the T_g, while it remains almost unchanged when aging in the deep glassy state. Although our observation is qualitatively consistent with previously reported results for other glasses, it remains difficult to conclude whether a 10% variation is physically significant. In future work, we will investigate a possible correlation between such variations and the macroscopic mechanical properties of epoxy glasses. To the best of our knowledge, no exiting theoretical model has attempted to predict the effect of aging on the size evolution of heterogeneous structures.

7. In line 190 I miss a reference to the glycerol data given.

We added reference 54 that is related to our discussion of the glycerol data in the revision. The modification is in red color. See line 12 on page 9.

8. In line 235 is referred to "an apparent percolating network" – is this important?

We removed the term "an apparent percolating network" to avoid an ambiguity in the revision. The modification is in red color. See lines 19,20 on page 11.

We agree that using the term "an apparent percolating network" is not necessary to describe the evolution of NMHs at this intermediate state.

9. In the discussion, it would be nice if the paper at the end in an outlook contemplates how far equilibration can proceed during long-time aging if only utilizing the beta process? In other words, do the authors expect that the alpha (main) and beta processes work in parallel or in series?

We extended the discussion regarding the prediction of long-time aging behavior of alpha and faster relaxation processes in PGs in the revision. The modification is in red color. See lines 7–11 on page 16.

Apparently, this is a very important question for gaining insights into the physics of glassy materials. Several recent theoretical models, such as *Phys. Rev. Lett. 134, 098203, 2025*, may provide guidance for understanding the contribution of alpha and faster relaxation processes to the long-time equilibration of glasses in the deep glassy state. However, experimentally observing this phenomenon at nanoscale remains highly challenging.

To reviewer #3:

Thank you very much for taking your time to read through our manuscript and to raise constructive comments, which are very helpful for us to improve our manuscript.

Responses to reviewer's comments:

Comments:

The manuscript addresses an important and timely problem in glassy materials: the structural origin of faster-than-α relaxation during deep physical aging. The combination of DSC, AM-FM AFM modulus mapping, and NCC-based tracking provides potentially significant real-space evidence for localized rearrangements of nanoscale mechanical heterogeneities. However, the authors should further substantiate the robustness of the AFM/NCC analysis, address possible surface and instrumental artifacts, improve statistical validation, and moderate several overstrong mechanistic claims.

Specific points

1. The manuscript repeatedly states or implies that the observed NMH evolution directly verifies the structural origin of the faster-than-α relaxation process. This conclusion is attractive, but the current data more directly show that local modulus heterogeneities evolve during aging, especially near Tg and, more weakly, deep in the glassy state. The link between these modulus changes and localized configurational rearrangements is plausible, but still interpretive. Likewise, the connection between the AFM-observed local evolution and the DSC-observed enthalpy recovery is correlative rather than fully causal. I suggest that the authors revise statements such as "direct evidence for the structural origin" or "verify the structural origin" to more cautious formulations. This adjustment would make the conclusions better aligned with the strength of the evidence.

We revised several expressions to ensure that our statements remain within the scope supported by the experimental evidence presented in the revision. The modification is in red color. See abstract, lines 25–31 on page 16.

2. The central evidence relies on long-duration AM-FM AFM modulus mapping. The authors acknowledge that the average modulus can be affected by small deviations in oscillation parameters, such as free amplitude and phase shift, over long waiting times, and therefore scale the modulus maps to their peak values before comparison. This treatment is understandable, but it also raises a concern: could the scaling procedure influence the modulus contrast and hence the calculated NCC/CE values? The authors should provide a sensitivity analysis showing that the main conclusions are not dependent on the specific normalization procedure.

We added a comparison of the NCC index mappings calculated from the original and scaled modulus images in the SI (Fig. S7), along with the corresponding discussion in the revision. The results demonstrate that the scaling has no effect on the NCC index mapping, and consequently, does not influence our main conclusions. The modification is in red color. See lines 11–14 on page 11.

3. The AFM measurements are performed on microtomed films transferred onto silicon substrates, whereas the DSC experiments reflect bulk enthalpic recovery. This raises an important question: to what extent do the observed NMH dynamics represent bulk polymer glass aging rather than surface or near-surface relaxation? If available, additional control experiments using different

film thicknesses, freshly prepared surfaces, or independently prepared specimens would strengthen the conclusions.

We added the discussion regarding a possible effect of sample preparation on the NMH dynamics in the revision. We also added the related work reported by Ediger and co-worker (Macromolecules 47, 471–478, 2014**) as references 51 to support our discussion.** The modification is in red color. See lines 20–31 on page 7 and 1–4 on page 8.

Because AFM measurements rely on the surface observations, the effects of surface and near surface characteristics are unavoidable. In polymer physics, particularly for thermoplastic polymers, surface and film-thickness effects are often associated with alterations in surface structure arising from factors such as changes in chain conformations and/or entanglement density compared with the bulk region (see, for example, *Macromolecules 47, 471–478, 2014*). In this study, we employed epoxy resin with a stable cross-linked network, which can help minimize such surface effects. Furthermore, the samples were prepared by microtome sectioning to expose the bulk region, thereby minimizing possible surface-induced changes in cross-linking density (e.g., due to the preferential segregation of uncured precursors toward the surface during curing).

We agree that the microtome-sectioning may introduce artificial nanoscale features on the sample surface. However, by comparing two types of samples, polystyrene and epoxy resin, our AM-FM AFM images shown in Fig. 2. demonstrate that the NMHs observed in the epoxy resin sample represent intrinsic heterogeneous structures of the material, rather than artifacts generated by the microtome-sectioning. In fact, similar structures have also been reported for epoxy resins prepared by fracture methods (see, for example, *J. Appl. Polym. Sci. 20, 2111, 1976*), indicating these heterogeneous structures are independent of the sample preparation method.

4. The representative AFM images and NCC maps are visually convincing, but the statistical basis of the conclusions is not yet sufficiently clear for a journal such as Communications Materials. The authors should provide more information on reproducibility, including: number of independent samples measured; number of different scanned regions analyzed; whether different AFM probes produced consistent results; error bars for average CE values; distributions of CE values, not only average CE; quantitative fraction of domains with CE < 0.5 as a function of aging time.

We added new data in Fig. S8 showing the quantitative comparison of the fraction of domains with $C_E \leq 0.5$ as a function of aging time at different T_a, and in Fig. S9 in the SI demonstrating the reproducibility of our AFM observations, along with the corresponding discussion in the revision. The modification is in red color. See lines 30–33 on page 11, 1–5 and 8–13 on page 12.

5. The DSC results show distinct enthalpy recovery features after aging near Tg and far below Tg, while the AFM observations show different patterns of NMH evolution under corresponding aging conditions. This combination is one of the strengths of the manuscript. However, the connection between these two measurements remains somewhat qualitative. The authors should clarify whether the same aging protocols, thermal histories, and sample conditions were strictly used for DSC and AFM measurements. More importantly, they should explain more carefully how the weak endothermic peak observed after deep aging is quantitatively or mechanistically related to the

small fraction of locally evolving NMHs observed by AFM. If possible, the authors could estimate whether the fraction or magnitude of local NMH evolution is consistent with the relative magnitude of the enthalpy recovery signal. Even a semi-quantitative discussion would improve the mechanistic coherence of the manuscript.

We added a quantitative comparison between DSC data and the fraction of domains with $C_E \leq 0.5$ at 303 and 358 K, along with corresponding discussion in the revision. The modification is in red color. See lines 26–29 on page 4, 1–5 on page 12, and 1–6 on page 18.

For a semi-quantitative comparison, we calculated the recovered enthalpy after a given aging time at a specific aging temperature T_a using Eq. (1) in the Methods. The recovered enthalpy after aging at 303 K for 24 h is ~0.43 Jg^{-1}, corresponding to about 14% of the value obtained after aging at 358 K for 24 h (~3.01 Jg^{-1}). This ratio is reasonably consistent with the much smaller fraction of domains having $CE \leq 0.5$ after aging at 303 K for 24 h (4%) than after aging at 358 K for 24 h (47%), as shown in Fig. S8. To facilitate a more quantitative comparison, both among the experimental results and with theoretical frameworks such as the collective small displacements model, additional experiments are required to systematically examine the effects of temperature and/or stress on the local rearrangements of NMHs under a broader range of aging conditions. However, such a comprehensive investigation is beyond the scope of the present work and will be addressed in future studies.

6. The manuscript discusses a "faster relaxation process beyond α relaxation." This is reasonable, but the terminology should be carefully controlled. It would be helpful for the authors to clarify whether they regard this faster process as related to β relaxation, Johari-Goldstein relaxation, collective small displacement processes, or a more general deep-glassy-state equilibration mode.

We added a discussion regarding the terminology of this faster relaxation process in the revision. The modification is in red color. See lines 7–12 on page 5.

Based on our experimental data, including AFM and DSC measurements, it remains difficult to conclusively identify this faster relaxation process as a β relaxation, Johari-Goldstein, collective small displacement, or slow Arrhenius processes. Although the latter appears to be more consistent with various experimental observations, including DSC and dielectric relaxation results, we prefer to use the term a "deep-glassy-state equilibration mode", as suggested by the reviewer to avoid unnecessary debate regarding its specific molecular origin.

7. The authors should more carefully justify the use of Hertzian contact mechanics for AM-FM modulus quantification. The epoxy glass is measured not only deep in the glassy state but also at 358 K, close to Tg. Under such near-Tg conditions, the material may exhibit appreciable viscoelasticity, adhesion, dissipation, and time-dependent contact response. Therefore, the AM-FM-derived modulus may be better described as an effective dynamic contact modulus rather than a purely elastic modulus. Since the main conclusion relies on the temporal evolution of local modulus contrast, the authors should discuss how possible deviations from the Hertzian elastic-contact assumption may affect the observed NMH evolution and the NCC analysis.

We added the discussion of the possible influence of dynamic effects on the NMH evolution near T_g in the revision. The modification is in red color. See lines 29–32 on page 8 and 1–3 on page 9.

We agree with the reviewer that, when measured at 358 K, near T_g, the obtained modulus maps might not represent the purely elastic modulus of the epoxy resin due to dynamic effects, such as viscoelasticity. It remains challenging for AFM measurements to quantitatively account for such dynamic effects in modulus mapping, regardless of whether the Hertzian model or other existing contact models, such as DMT or JKR, are applied. However, we suppose these dynamics effects are primarily governed by the segmental dynamics of the epoxy resin. Since the relaxation time at 358 K, about 14 K below the T_g, should be relatively longer than the scanning time for each image (~64 s), these effects are expected to not significantly influence the modulus contrast of local NMHs within each image.

8. The expression "localized ensembles of loosely packed atoms" is not fully appropriate for the present epoxy polymer glass. This terminology seems to originate from studies of metallic or atomic glasses, whereas the relevant structural units in a cross-linked epoxy network are polymer segments, network strands, or local segmental packing motifs. The authors themselves later discuss the CSD model in terms of segmental movements and local segmental packing, which is more consistent with the polymeric nature of the system. I suggest replacing "loosely packed atoms" with terms such as "loosely packed molecular segments," "localized segmental ensembles," or "locally less constrained molecular packing" throughout the manuscript. This would avoid conceptual ambiguity and make the proposed relaxation mechanism more precise.

We corrected this phrase to be consistent with the polymer structure in the revision. The modification is in red color. See lines 2 and 8 on page 3, lines 14, 15 on page 15.

Several minor comments

1. There are several typographical and wording errors that should be corrected. For example, "NNC" should be "NCC" in several figure captions; "tract" should be "track"; "Nevetherless" should be "Nevertheless"; "species" should likely be "pieces" in the sample preparation section.

We corrected these errors in the revision. The modification is in red color. See lines 6 and 20 on page 8, line 13 on page 17, and in Captions of Figs. 4,5.

2. The manuscript should consistently use either "normalized cross-correlation" or "NCC" after the first definition.

We corrected this phrase in the revision. The modification is in red color. See lines 25,26 on page 19.

3. The sentence "the evolution of NMHs become much faster" should be revised to "the evolution of NMHs becomes much faster."

We corrected this phrase in the revision. The modification is in red color. See line 17 on page 12.

4. The authors should define CE clearly when it first appears in the Results section. Although NCC is introduced in the Methods, the distinction between C, CE, CH, and average CE should be made more transparent for readers.

We added the definition of C_H and C_E into the main text and Figs. 4 and 5 captions in the revision. The modification is in red color. See lines 14–17 on page 11.

5. The authors should avoid overusing phrases such as "nicely consistent" and "compelling evidence." A more neutral scientific tone would improve the manuscript.

We modified these phrases in the revision. The modification is in red color. See line 28 on page 16.

6. The phrase "in deep within the glassy state" should be revised to "deep within the glassy state."

We corrected this phrase in the revision. The modification is in red color. See line 13 on page 15.