

Chemical Functionalities Govern Polyamide–Alumina Adhesion through Local Conformational Dynamics

Corresponding Author: Professor Takuya Kuwahara

This file contains all editorial decision letters in order by version, followed by all author rebuttals in order by version.

Version 0:

Decision Letter:

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Dear Professor Kuwahara,

Thank you for submitting your manuscript, "Chemical Functionalities Govern Polyamide–Alumina Adhesion through Local Conformational Dynamics", to Communications Materials. It has now been seen by 3 referees, whose comments are appended below. You will see that while they find your work of interest, some important points are raised. We are interested in the possibility of publishing your study in Communications Materials, but would like to consider your response to these concerns in the form of a revised manuscript before we make a decision on publication.

In particular, the Reviewers request that you make the advance over previous studies and methodologies clear, in addition to providing further experimental metrics, and modifying Fig 7g.

We therefore invite you to revise and resubmit your manuscript, taking into account the points raised.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

When submitting your revised manuscript, please include the following:

-A response letter with a point-by-point reply to each of the referee comments and a description of changes made. Please include the complete referee report in the response letter. Please note that the response letter must be separate to the cover letter to the editors.

-A marked-up version of the manuscript with all changes to the text in a different colored font. Please do not include tracked changes or comments. Please select the file type 'Revised Manuscript - Marked Up' when uploading the manuscript file to our online system.

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In particular, the Data availability statement should include:

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- Other unique identifiers (such as DOIs and hyperlinks for any other datasets)

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We hope to receive your revised paper within six weeks; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we will close your file. In this event, we will still be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Materials or published elsewhere in the meantime.

Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Dr Jet-Sing Lee
Senior Editor
Communications Materials
orcid.org/0000-0002-6740-8700

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

Dear Editor,

The manuscript authored by T. Yoshida et al. provides a comprehensive computational study regarding the behavior of polyamides (PAs) adsorbed into alumina substrates under tensile strain. The authors examine in detail the properties of different PAs adsorbed chains via atomistic molecular dynamics (MD) simulations.

Overall, the manuscript is generally well written, and the simulations are thoroughly analyzed. The subject is of significant interest and the reported findings could be useful to the community. However, there are several key concerns that do not allow publication of the manuscript in its current form.

A) My primary concern pertains to the novelty of the presented data. The behavior of polymer chains adsorbed onto inorganic or metallic substrates has been extensively investigated in prior studies using atomistic MD simulations. For example, the main message of the current work, that chemical functionalities affect the structure (density and conformations) and dynamics of polymer chains, is well established in the literature. It is surprising that the authors omit discussion of many foundational and recent studies in this area. For instance, relevant works on confined polymers and polymer nanocomposites include:

Macromolecules (2020), 53, 6173; Fluid Phase Equilib. (2021), 536, 112966; J. Appl. Polym. Sci. (2021), 138, 49755; Macromolecules (2023), 56, 6552; Nano Lett. (2024), 24, 148 and references within.

I would recommend authors to perform a thorough discussion of previous works in the field, and related their findings to existing knowledge in it.

B) Authors perform a detailed, albeit rather standard, analysis of the behavior of density and chain conformations at the PS/alumina interface, under tensile deformation. Several topics which are very important for polymer/metal interfacial

systems could be considered to significantly strengthen the manuscript as for example:

1) Heterogeneous mechanical and dynamical behavior of polymer/metal interfaces: It is well known that confined polymer systems exhibit spatially heterogeneous mechanical behavior. In particular, attractive polymer/metal interfaces typically lead to a rigid interfacial layer. This has been studied using a variety of approaches (e.g., Phys. Rev. E (2020), 102, 030501; J. Phys. Chem. B (2022), 126, 7429). Incorporating such considerations would enhance the relevance and depth of the manuscript.

2) Interfacial width: The simulation data could be further analyzed to provide information about the dependence of the width of the polymer/metal interface on the applied tensile deformation.

C) Several important aspects of atomistic simulations of polymers should be more thoroughly addressed:

1) The equilibration of long polymer chains is a highly non-trivial issue. Authors could provide standard metrics (as for example internal distances plots, decorrelation of the end-to-end distance) to exhibit the proper equilibration of model atomistic chains.

2) Moreover, it is not clear what the effect of temperature is on the two chosen PAs. Are the current simulation temperatures of PA6 and PAMXD6 equidistant from their corresponding glass transition temperatures? If not, then potential differences in their mechanical behavior for this reason should be discussed in the manuscript.

3) The cooling rates used to prepare the model systems are quite large. It would be interesting to investigate the effect of them on the structure of the resulting PA/metal interface.

D) Another crucial point for all atomistic models of polymer chains confined between metal substrates is the polymer/metal interaction. It is well known that typical mixing rules cannot predict accurately the complex physicochemical phenomena at the polymer/metal interface. On the contrary, systematic approaches based on the parametrization of (classical) atomistic atom/atom interactions between polymer chains and metal substrates based on ab-initio calculations allow the development of accurate atomistic models, see for example: J. Phys. Chem. C (2022), 126, 16792–16803.

E) Continuing from the above point and given that the authors have already performed DFT calculations, it would be informative to compare the predicted adsorption energies and conformations with those obtained from the atomistic force field. If significant discrepancies exist, the reliability of the current PA/alumina model should be reconsidered or further justified.

F) Furthermore, to quantify the conformational changes of adsorbed chains a local radius of gyration is used. The results are interesting but there is no information about the anisotropic shape of polymer chains. Other metrics involving the local radius of gyration tensor and the asphericity ratio would be more useful.

G) Last, but not least, the value of this work would be greatly enhanced by comparing, if possible, the predictions of the CG model with experimental data, if feasible. For example, experimental data on interfacial thickness, chain orientation, or mechanical behavior could help validate the atomistic predictions presented in the manuscript.

Reviewer #2 (Remarks to the Author):

This manuscript provides a molecular-level understanding of the adsorption phenomena at the polymer/ Al_2O_3 interface by introducing segment-scale analysis. The following minor comments are provided for the authors' consideration:

1. "These differences observed in the S–S behavior of..."

The discussion centers around localized deformation and void formation. However, Fig. 3 is based on displacement, and strictly speaking, displacement from the initial configuration does not directly represent local deformation. Previous studies have addressed similar phenomena using local strain and free volume as indicators. The authors are encouraged to cite and consider the methodology used in the following reference:
<https://doi.org/10.1016/j.commatsci.2023.112333>

2. Regarding the definition of local radius of gyration

It is expected that the local radius of gyration approaches the normal radius of gyration as the segment length s increases. However, in Fig. 7, R_g appears to increase monotonically without saturation. Does this imply that the range of s used is significantly smaller than the full chain length? Please clarify the scale of s in relation to the total chain length.

3. On Fig. 7g

The figure is somewhat difficult to interpret and would benefit from improvement. Given that the definition of R_g captures local structural features, the absolute values are expected to show only small changes, making absolute comparisons less informative. Rather than emphasizing the magnitude of R_g , it would be more meaningful to clearly indicate how each chain segment—classified as train, loop, or tail—evolves during deformation. The current visualization does not readily convey this transition.

4. Regarding MD boundary conditions

The manuscript states that periodic boundary conditions are applied in all three spatial directions. For slab-type systems like this, it is well known that spurious dipole interactions may arise due to artificial periodicity in the z -direction. In such cases, dipole corrections (e.g., `kpspace_modify slab` in LAMMPS) are often applied. Did the authors implement this correction? If not,

there may be non-negligible artifacts from periodic images. Please consider the following reference for more details:
<https://doi.org/10.1063/1.479595>

Reviewer #3 (Remarks to the Author):

This manuscript compares the adsorption behavior and high-strain conformational evolution of the linear aliphatic PA6 versus the aromatic PMXD6 on both OH-terminated and non-terminated α -Al₂O₃(0001) surfaces. Through all-atom MD simulations, three key conformational modes are identified, and DFT adsorption-energy calculations offer the physicochemical basis for the desorption mechanisms observed in MD. The manuscript is logically organized with sound analysis. Some suggestions are provided below:

1. Please explicitly state that Δz represents the absolute value of the coordinate difference.
2. Cite the original experimental and/or simulation studies that established 0.45 nm as the adsorption cutoff to justify its use.
3. Explain how the uniaxial strain rate of $6.4 \times 10^{-6} \text{ fs}^{-1}$ was determined. Provide the theoretical rationale or reference prior work.
4. Because PA6 and PMXD6 contain different numbers of backbone atoms per monomer, it might be more reasonable to normalize the average segment length (s).
5. To substantiate claims like "the oxygen atoms are oriented toward the surface," it would be necessary to include a quantitative metric of amide orientation, such as the angle between the C=O bond vector and the surface normal.
6. In Fig. 7g, assign distinct colors so that the $\epsilon z = 0.0$ and $\epsilon z = 0.2$ curves can be easily distinguished, and ensure train/loop/tail each has their unique color for visual purpose (the current plot uses red for both $\epsilon z = 0.2$ and "tail," which should be corrected).

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Version 1:

Decision Letter:

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Dear Professor Kuwahara,

Thank you again for submitting your revised manuscript "Chemical Functionalities Govern Polyamide–Alumina Adhesion through Local Conformational Dynamics" to Communications Materials. We have now received reports from the 3 reviewers, whose comments are pasted below. They have raised important points which must be addressed in a revised manuscript.

In particular, Reviewer 1 raises several technical issues that need to be addressed. You will also see that Reviewer 1 comments that they don't feel the paper is appropriate for Nature Communications - while Communications Materials is not as editorially selective as Nature Communications, we do ask that you respond to the two criticisms that Reviewer 1 raises regarding advance over previous works.

To allow us to move forward with your work, we also ask that you edit your manuscript according to the attached table.

Please read this document carefully as we will be unable to further assess your revised paper until these important points are addressed.

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- A clean version of your revised manuscript with no mark-ups
- A marked-up version of your paper with all changes highlighted in a different colour

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We hope to receive your revised paper within six weeks, but we understand that the revisions may take longer. Please let us know if you find that the revision process will take substantially more time.

We are committed to providing a fair and constructive peer-review process. Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

John Plummer, PhD
Chief Editor
orcid.org/0000-0003-4824-8497
Communications Materials

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

I am glad to see that Authors considered most of my comments in the revised draft. Nevertheless, I still have major concerns regarding its suitability for publication in a broad high impact factor journal such as Nature Communications.

My primary concern remains the novelty of the presented data. For instance, Authors claim that “we would like to emphasize that the key novelty of our study lies in the introduction of the local radius of gyration (R_g^L) as a segmental-scale structural descriptor”. This claim is not accurate as the structure of polymer chains at interfaces via several metrics, including local radius of gyration, has been extensively investigated over the past decades within the simulation community.

Similarly, the Authors argue that the use of all-atom is essential to capture interfacial behavior, stating that “our all-atom MD study highlights the critical role of chemical functionalities in both PA chains and Al₂O₃ surfaces, which are absent in typical coarse-grained” While this point is valid, it is a bit generic since the necessity of atomistic resolution for capturing interfacial phenomena has already been well established in the literature.

Below I provide additional, more specific technical comments:

1) Equilibration of polymeric systems (Previous comment C): Authors add a new section (S11, Figure 13) discussing the relaxation state of the amorphous structure. As expected, there is not any relaxation at 300K since the system is in glassy state, so there is no point in presenting the end-to-end vector autocorrelation function that remains constant at one during time.

The critical question is whether the systems are well relaxed at higher temperatures. The internal distance data (Fig. 13b) do not display the Gaussian statistics typical of well-relaxed conformations, which indicates insufficient equilibration. This could have unclear effects on the predicted mechanical properties of the systems. Given the additional challenges of equilibrating interfacial conformations, it is even more questionable whether the interfacial layer is adequately relaxed, i.e., i.e. that its structure is not strongly dependent on the history of the system, such as the cooling rate and the initial, rather unrealistic high, temperature of 1000K.

The above issues can be investigated by different cooling protocols, involving (much) longer MD simulations and statistics over multiple uncorrelated configurations.

2) DFT calculations and validation of AA FFs (Section S6): Authors present in Supplementary Figures 6 and 7 results related to the "Adsorption geometries and energies of PA monomers on the OH- and non-terminated Al₂O₃ surface using DFT and MD calculations". First, it is not clear how we can compare adsorption energies (and geometries) at zero temperature (DFT data) with data from MD simulations which include entropic contributions and are closer to free energies of adsorption. Second, the reported values are only qualitatively similar and quantitatively differ substantially. This strongly suggests that the force field is at best qualitatively adequate and does not justify the claim that "the FF used in this study reasonably captures the interfacial dynamics, supporting the reliability of our atomistic model."

3) New Section S9 (Supplementary Figures 10, 11): The statistics related to the values of local radius of gyration tensor components are rather poor. I recommend performing simulations of multiple independent configurations to strengthen the reliability of these findings.

4) In the new section related to the glass transition temperature (S14. Effect of the difference between glass transition temperatures and MD simulation temperature) to demonstrate that the simulations were performed in the glassy regime, authors compute the mean squared displacements (MSDs) at 300 K and 1 atm over 10 ns (Supplementary Fig. 16c). MSDs naturally provide important information about the mobility of polymer chains, but it is not straightforward to relate this information with the actual T_g. more reliable approach would be to compute T_g from a "density vs. temperature" analysis via simulations across a range of temperatures. In addition, the presented MSD curves do not clearly exhibit the plateau-like behavior characteristic of glassy systems.

Reviewer #2 (Remarks to the Author):

Each comment has been responded to appropriately.

Reviewer #3 (Remarks to the Author):

The authors have made adequate revision to address reviewers' comments.

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Version 2:

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Dear Professor Kuwahara,

Thank you once again for submitting your manuscript, "Chemical Functionalities Govern Polyamide–Alumina Adhesion through Local Conformational Dynamics," to Communications Materials. The concerns of our reviewers have been addressed, but there are some amendments needed before we can accept your paper.

We ask that you edit your manuscript according to the attached table. **Please read this document carefully as we will be unable to further assess your revised paper until these important points are addressed.**

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Best regards,

John Plummer, PhD
Chief Editor
orcid.org/0000-0003-4824-8497
Communications Materials

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Point-by-point response to the reviewers' comments

We thank all three reviewers for their substantial efforts to evaluate our manuscript as well as their positive assessments. Their constructive and insightful comments were very important to perform additional simulations and experiments and improve the presentation and discussion of our results substantially. Please see our replies in black here below as well as the changes marked in red below and in the revised manuscript and Supplementary Information.

Reviewer #1:

The manuscript authored by T. Yoshida et al. provides a comprehensive computational study regarding the behavior of polyamides (PAs) adsorbed into alumina substrates under tensile strain. The authors examine in detail the properties of different PAs adsorbed chains via atomistic molecular dynamics (MD) simulations. Overall, the manuscript is generally well written, and the simulations are thoroughly analyzed. The subject is of significant interest and the reported findings could be useful to the community. However, there are several key concerns that do not allow publication of the manuscript in its current form.

We sincerely appreciate the reviewer's fruitful comments and suggestions. These helped us improve the clarity and quality of the manuscript significantly. We have carefully addressed all points raised and revised the manuscript accordingly.

A) My primary concern pertains to the novelty of the presented data. The behavior of polymer chains adsorbed onto inorganic or metallic substrates has been extensively investigated in prior studies using atomistic MD simulations. For example, the main message of the current work, that chemical functionalities affect the structure (density and conformations) and dynamics of polymer chains, is well established in the literature. It is surprising that the authors omit discussion of many foundational and recent studies in this area. For instance, relevant works on confined polymers and polymer nanocomposites include: *Macromolecules* (2020), 53, 6173; *Fluid Phase Equilib.* (2021), 536, 112966; *J. Appl. Polym. Sci.* (2021), 138, 49755; *Macromolecules* (2023), 56, 6552; *Nano Lett.* (2024), 24, 148 and references within. I would recommend authors to perform a thorough discussion of previous works in the field, and related their findings to existing knowledge in it.

Reply:

We thank the reviewer for the constructive comment and for providing several important papers. As the reviewer mentioned, many of these works have thoroughly investigated the behavior of polymer chains adsorbed on inorganic or metallic substrates primarily under isothermal and isobaric equilibrium conditions, often employing united-atom or coarse-grained models. In particular, recent studies by Prof. Harmandaris and co-workers (e.g. Reda et al., *JPCB* 2022, 126, 7429-7444; Reda et al., *Nano Lett.* 2024, 24, 148-155) have provided valuable insights into the non-equilibrium dynamics of confined polymers under tensile deformation. We found their analysis techniques, such as interfacial density profiles and heterogeneous stress distributions in train, loop, and tail segments, highly informative. Thus, we have incorporated similar analyses into the revised manuscript and Supplementary Information to better contextualize our findings.

At the same time, we would like to emphasize that the key novelty of our study lies in the introduction of the local radius of gyration $\langle R_g^L \rangle$ as a segmental-scale structural descriptor (as shown in Fig. 7). This metric enabled us to uncover three distinct conformational modes—tail elongation, loop-to-tail transition, and chain desorption—which collectively govern the macroscopic joining strength of PA-Al composites. We believe this per-segment conformational metric provides a valuable link between local structure and interfacial mechanics, which has not been addressed previously. Moreover, our all-atom MD study highlights the critical role of chemical functionalities in both PA chains and Al_2O_3 surfaces, which are absent in typical coarse-grained models, in local conformational dynamics of adsorbed PA chains especially in non-equilibrium conditions. Indeed, all-atom MD by Heydari et al. revealed the effect of oxygen functional groups on the structure of the adsorption layer. However, it was limited to equilibrium states and did not analyze polymer conformations in detail. In contrast, detailed analyses in this study elucidate how chemical functionalities govern both non-equilibrium conformational dynamics and nano-mechanics of polymer chains. We have now cited all references suggested by the reviewer in the Introduction and Discussion section, and added the following sentences in the Discussion section of the revised manuscript. We hope these modifications clarify the novelty and significance of our contribution.

Added to page 3:

“The mechanical properties of polymers are governed by characteristic parameters such as entanglement length and time scales¹⁸, radius of gyration¹⁹, and crystallinity¹⁵. Harmandaris and co-workers have extensively performed united-atom molecular dynamics simulations of polymer/nanoparticle composites under tensile strain²⁰, in combination with continuum models^{21,22}. Their studies revealed heterogeneous strain fields near their interface by analyzing the conformational dynamics and atomic-level stresses of train, loop, and tail segments in adsorbed polymer chains, which strongly influence mechanical properties.”

Added to page 3:

“Equilibrium AA-MD simulations demonstrated that oxygen-containing functional groups in polymer chains and solid surfaces play a critical role in the formation of adsorption layers and their adhesion to metal²⁵ and graphene surfaces²⁶.”

Added to page 4:

“These results shed light on the segmental length scales that govern conformational changes in adsorbed PA chains and reveal three distinct modes—tail elongation, loop-to-tail transition, and chain desorption—that contribute to the macroscopic adhesion strength of PA/Aluminum composites.”

Added to page 15:

“The effects of chemical functionalities in polymer chains on their conformational dynamics under tensile strain and the resulting mechanical properties have not been fully addressed in previous AA-MD simulations²⁵.”

Added to page 15-16:

“While the static conformations of polymer chains adsorbed on solid surfaces have been extensively characterized²⁹, only a few MD studies²⁰ have investigated their dynamic response under tensile strain and its correlation with interfacial bonding strength. While relaxation

dynamics of adsorbed chains have been explored using united-atom models^{30,31}, atomic-level understanding of the conformational dynamics during tensile deformation and how they influence polymer/metal adhesion remains limited. To bridge this knowledge gap, we introduced the local radius of gyration as a tool to quantify localized conformational changes of adsorbed PA chains, integrating it with full-atom modeling. This approach enabled us to identify three distinct conformational modes of polymer chains that dominate the adhesion of PA to Al₂O₃ surfaces. This metric can also be extended to other polymers, providing insights into conformational modes and their evolution under mechanical loading.”

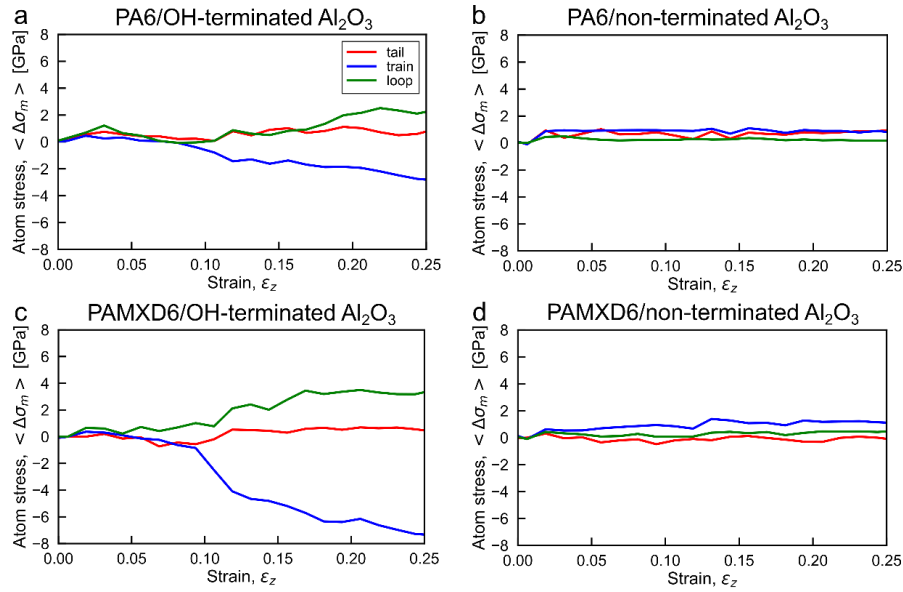
B) Authors perform a detailed, albeit rather standard, analysis of the behavior of density and chain conformations at the PS/alumina interface, under tensile deformation. Several topics which are very important for polymer/metal interfacial systems could be considered to significantly strengthen the manuscript as for example: 1) Heterogeneous mechanical and dynamical behavior of polymer/metal interfaces: It is well known that confined polymer systems exhibit spatially heterogeneous mechanical behavior. In particular, attractive polymer/metal interfaces typically lead to a rigid interfacial layer. This has been studied using a variety of approaches (e.g., Phys. Rev. E (2020), 102, 030501; J. Phys. Chem. B (2022), 126, 7429). Incorporating such considerations would enhance the relevance and depth of the manuscript.

Reply:

We thank the reviewer for the constructive suggestion. The paper by Reda et al. (J. Phys. Chem. B 2022, 126, 7429) indeed motivated us to investigate spatially heterogeneous mechanical responses near the interface by analyzing per-atom stresses in the adsorbed polymer chains during tensile deformation. We computed the von Mises atomic stress using the per-atom stress tensor and Voronoi tessellation methods implemented in LAMMPS. Supplementary Figure 8 shows the evolution of the average change in von Mises stress $\langle \Delta \sigma_m \rangle$ for atoms classified as tail, train, and loop segments for all four systems. Here, $\langle \Delta \sigma_m \rangle$ is defined as the difference in $\langle \sigma_m \rangle$ at a given tensile strain ε_z relative to that at $\varepsilon_z = 0$, following the literature. Interestingly, on the OH-terminated surface, $\langle \Delta \sigma_m \rangle$ for train segments decreases sharply at higher strains (after yielding), indicating stress release due to chain desorption and subsequent local structural relaxation. In contrast, on the non-terminated surface, $\langle \Delta \sigma_m \rangle$ remains relatively constant, suggesting that adsorbed chains maintain entanglement and resist desorption. This analysis underscores the spatially heterogeneous stress evolution within the adsorption layer and supports the desorption-driven stress relaxation mechanism. We have added a sentence to page 10 of the revised manuscript and Supplementary Fig. 8.

Added to page 10:

“Corresponding changes in the von Mises atomic stress of the tail, train, and loop segments are shown in Supplementary Fig. 8, indicating that molecular desorption induces local stress relaxation within the adsorption layer.”



Supplementary Figure 8. Evolutions of averaged von Mises atomic stress ($\Delta\sigma_m$) of backbone atoms classified as train, loop, and tail segments during tensile deformation: a) PA6/OH-terminated Al_2O_3 , b) PA6/non-terminated Al_2O_3 , c) PAMXD6/OH-terminated Al_2O_3 , and d) PAMXD6/non-terminated Al_2O_3 . $\Delta\sigma_m$ is defined as the difference in $\langle\sigma_m\rangle$ at a given strain ε_z relative to that at $\varepsilon_z = 0$.

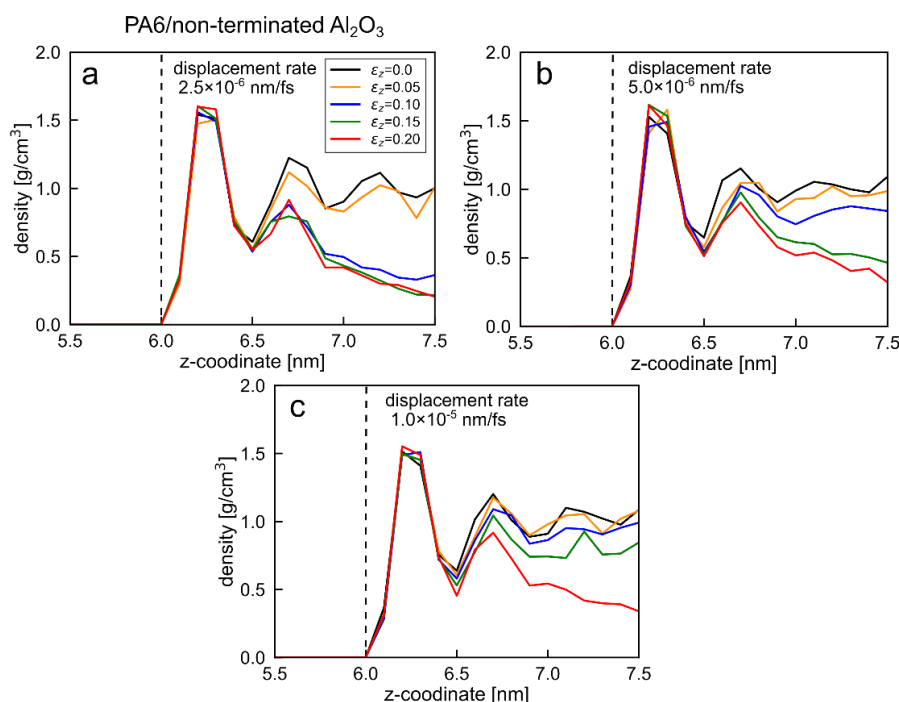
2) Interfacial width: The simulation data could be further analyzed to provide information about the dependence of the width of the polymer/metal interface on the applied tensile deformation.

Reply:

We thank the reviewer for the helpful suggestion. Inspired by the approach in Reda et al. (J. Phys. Chem. B 2022, 126, 7429), we analyzed how tensile deformation and strain rate affect the interfacial density profile in the PA6/non-terminated Al_2O_3 system. Supplementary Figure 4 shows the evolutions in the density profiles at three strain rates of 2.5×10^{-6} , 5.0×10^{-6} (used in the main text), and $1.0 \times 10^{-5} \text{ nm fs}^{-1}$. The results show that the thickness of the first adsorption layer is not affected by both tensile strain and strain rate. However, the valley between the first and second density peaks (at $z \approx 6.5 \text{ nm}$) becomes more pronounced with increasing strain and at lower strain rates. This may be due to insufficient relaxation time of polymer chains in the adsorption layer at higher strain rates. Moreover, large strains enhance density decreases in the second adsorption layer at lower strain rates (Supplementary Fig. 4a). In contrast, at the higher strain rate of $1.0 \times 10^{-5} \text{ nm fs}^{-1}$ (Supplementary Fig. 4c), such decreases are suppressed. We have added Supplementary Fig. 4 to the revised Supplementary Information and the following sentence to page 7 of the revised manuscript.

Added to page 7:

“Evolutions of the density profile of the PA6/non-terminated Al_2O_3 system under different strain rates are shown in Supplementary Fig. 4, indicating that lower strain rates enhance local structural relaxation in the second layer at $z = 6.7 - 7.5 \text{ nm}$.”



Supplementary Figure 4. Evolutions of the density profile of the PA6/non-terminated Al_2O_3 system at different strain rates: a) 2.5×10^{-6} , b) 5.0×10^{-6} , and c) $1.0 \times 10^{-5} \text{ nm fs}^{-1}$.

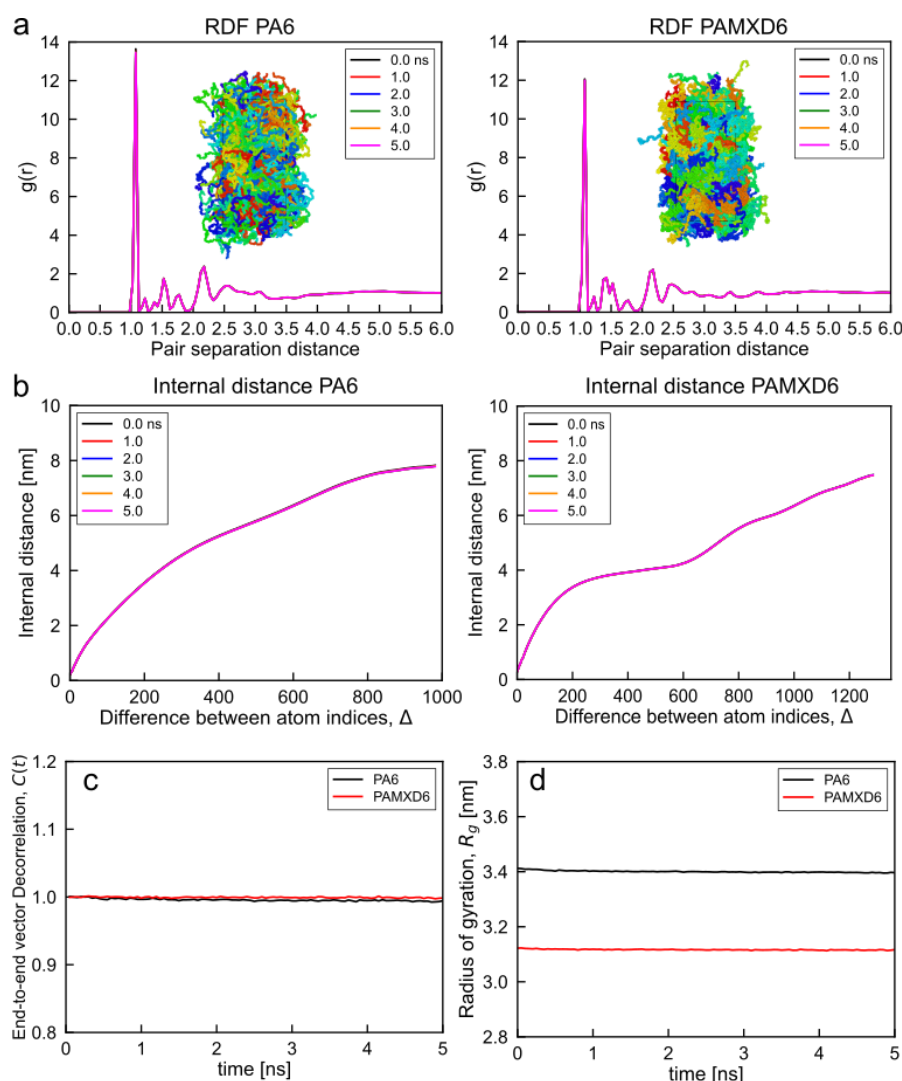
C) Several important aspects of atomistic simulations of polymers should be more thoroughly addressed: 1) The equilibration of long polymer chains is a highly non-trivial issue. Authors could provide standard metrics (as for example internal distances plots, decorrelation of the end-to-end distance) to exhibit the proper equilibration of model atomistic chains.

Reply:

We greatly appreciate the critical comment. To confirm that our atomistic PA chains were properly equilibrated, we performed standard structural analyses including the radial distribution function (Supplementary Fig. 13a), internal distance profiles (Supplementary Fig. 13b), end-to-end vector decorrelation (Supplementary Fig. 13c), and radius of gyration (Supplementary Fig. 13d). After 1-ns NPT simulations at 1000 K and 1 atm, we quenched the PA melts to 300 K at a rate of 1 K ps^{-1} , followed by 10-ns NPT simulations at 300 K and 1 atm. All metrics remain stable throughout the 10-ns runs, confirming the structural equilibration of our amorphous PA and PAMXD6 models. We have added Supplementary Fig. 13 to the revised Supplementary Information and the following sentence to page 18 of the revised manuscript.

Added to page 18:

“Subsequently, we performed 0.5-ns simulations at 300 K and 1 atm. To ensure equilibration, we extended the simulation time to 10 ns and analyzed the evolution of the radial distribution function, internal distance, end-to-end vector decorrelation, and radius of gyration (Supplementary Fig. 13). All metrics remain stable throughout the 10-ns runs, confirming the structural equilibration of our amorphous PA and PAMXD6 models.”



Supplementary Figure 13. Structural analysis of amorphous PA6 and PAMXD6. a) Radial Distribution Function (RDF). **b)** Internal distance. **c)** End-to-end vector decorrelation. **d)** Radius of gyration.

2) Moreover, it is not clear what the effect of temperature is on the two chosen PAs. Are the current simulation temperatures of PA6 and PAMXD6 equidistant from their corresponding glass transition temperatures? If not, then potential differences in their mechanical behavior for this reason should be discussed in the manuscript.

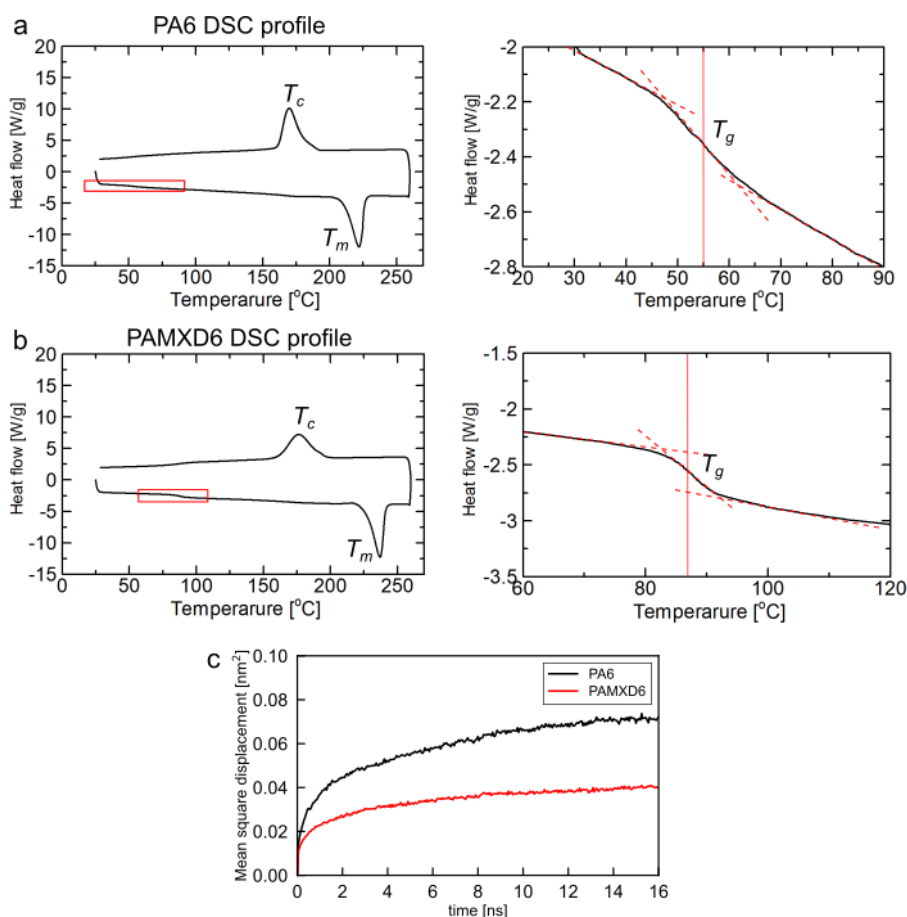
Reply:

Thank you for raising this important point. Since no experimental data was available for the glass transition temperature T_g of PAMXD6, we experimentally determined the glass transition temperatures of PA6 and PAMXD6 using differential scanning calorimetry (DSC Q2000, TA Instruments Inc.). DSC measurements were performed by heating the samples from 25 °C to 260 °C at 10 °C min⁻¹ and cooling back to 25 °C at a rate of 10 °C min⁻¹. To eliminate the effects of absorbed moisture, T_g was taken from the second heating/cooling cycle. The resulting T_g values were equal to 55.0 °C for PA6 (Supplementary Fig. 16a) and 87.3 °C for

PAMXD6 (Supplementary Fig. 16b). This confirms that the simulation temperature of 300 K lies well below T_g of both PA6 and PAMXD6 ($\Delta T = -28.2$ °C for PA6 and -60.5 °C for PAMXD6). Next, to verify that the simulations were performed in the glassy regime, we computed the mean squared displacements (MSDs) at 300 K and 1 atm over 10 ns (Supplementary Fig. 16c). The MSDs of both PA6 and PAMXD6 remain very small (< 0.07 nm²), indicating that both PA6 and PAMXD6 are well below their T_g and exhibit minimal chain mobility. We have added Supplementary Fig. 16 to the revised Supplementary Information and the following sentence to page 18-19 of the revised manuscript.

Added to page 19:

“Differential scanning calorimetry measurements confirmed that the simulation temperature of 300 K is well below the glass transition temperatures of both PA6 and PAMXD6. Mean squared displacements computed from 16-ns MD runs at 300 K and 1 atm also indicate minimal chain mobility, verifying that our simulations of both PAs were conducted in the glassy state (Supplementary Fig. 16).”



Supplementary Figure 16. Differential scanning calorimetry measurements of a) PA6 and b) PAMXD6. Evolution of mean squared displacements of c) PA6 and PAMXD6 computed from 16-ns MD simulations at 300 K and 1 atm.

3) The cooling rates used to prepare the model systems are quite large. It would be interesting to investigate the effect of them on the structure of the resulting PA/metal interface.

Reply:

We agree that the quench rate is an important parameter in polymer modeling. To assess its influence, we prepared a PA6 sample using a lower quench rate of 0.1 K ps^{-1} (compared to 1 K ps^{-1} used in the main text). Figure R1 shows a comparison of the stress-strain curves of PA6 samples prepared using the different quench rates. The resulting stress-strain curves are essentially unchanged. Both the maximum tensile stress and interfacial responses, including local inhomogeneous displacements after yielding, remain nearly identical. Within the computationally feasible range, the quench rate does not significantly affect the interfacial structure or mechanical behavior. We have added the following sentence to page 7 of the revised manuscript and the results at 0.1 K ps^{-1} to Supplementary Fig. 3 of the revised Supplementary information.

Added to page 7:

“A brief discussion on the effect of quench rate is provided in Supplementary Fig. 3, demonstrating that the stress-strain behavior is largely unaffected within the computationally accessible range of quench rates.”

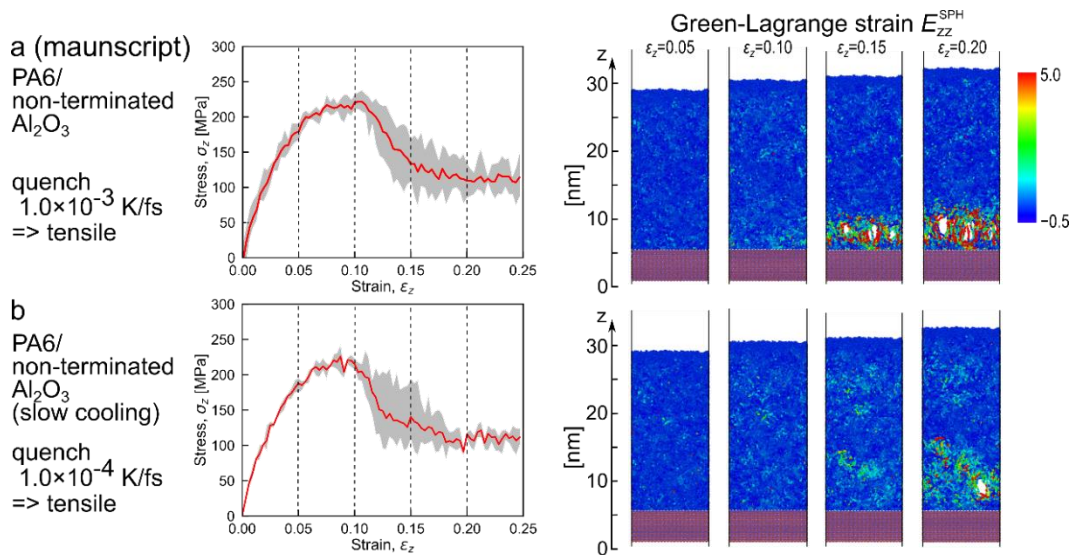


Figure R1. Stress-strain curves and snapshots of Green-Lagrange strain E_{zz}^{SPH} in the PA6/non-terminated Al_2O_3 system at different quench rates: a) 1.0 (used in the main text) and b) 0.1 K ps^{-1} .

D) Another crucial point for all atomistic models of polymer chains confined between metal substrates is the polymer/metal interaction. It is well known that typical mixing rules cannot predict accurately the complex physicochemical phenomena at the polymer/metal interface. On the contrary, systematic approaches based on the parametrization of (classical) atomistic atom/atom interactions between polymer chains and metal substrates based on ab-initio calculations allow the development of accurate atomistic models, see for example: J. Phys. Chem. C (2022), 126, 16792–16803.

Reply:

We agree that reparameterization of FF interactions based on DFT calculations can improve

accuracy in describing complex interfacial phenomena. The reference provided by the reviewer offers a comprehensive computational framework for developing such refined FFs. Before doing so, as suggested in the reviewer's subsequent comment, we have evaluated the adsorption energies of PA monomers on Al_2O_3 using FFs used in this study and compared them with DFT results. We found that both results are in good agreement. Zhao et al. also successfully applied the same FFs parameters to PA6/ Al_2O_3 systems (Appl. Surf. Sci. 2024, 656, 159694). Therefore, we added the comparison of adsorption energies between FF and DFT to the revised Supplementary Information and added a remark on the limitations of mixing rules and future FF refinement to page 17 of the revised manuscript.

Added to page 17:

"We used the Lorentz–Berthelot mixing rules to compute non-bonded cross interactions. While such conventional mixing rules have known limitations, a systematic approach to explicitly parameterize LJ interactions for polymer-metal systems using DFT calculations has recently been proposed^{30,35,36}. In the present study, however, the PA/ Al_2O_3 interactions were found to be reasonably well described well by the current FFs. Further refinement of cross-interaction parameters will be addressed in future work."

E) Continuing from the above point and given that the authors have already performed DFT calculations, it would be informative to compare the predicted adsorption energies and conformations with those obtained from the atomistic force field. If significant discrepancies exist, the reliability of the current PA/alumina model should be reconsidered or further justified.

Reply:

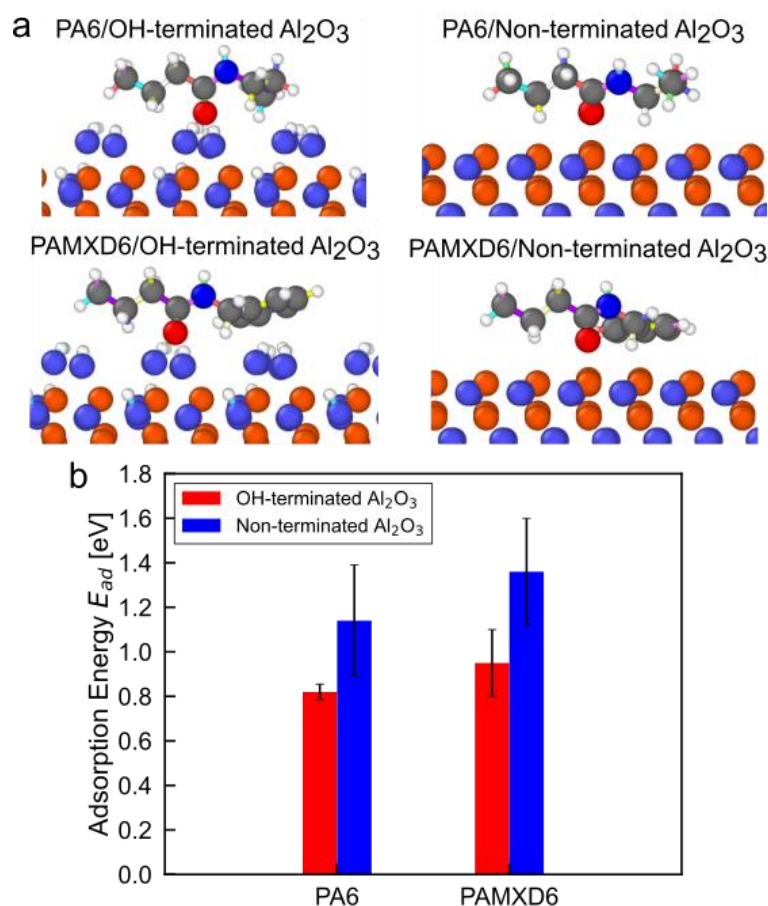
We appreciate this constructive suggestion. To evaluate the accuracy of the classical FF used in this study, we compared the adsorption energies obtained from FFs with those from DFT calculations. Supplementary Figure 7 shows the FF adsorption configurations and energies of PA6 and PAMXD6 monomers on both OH- and non-terminated Al_2O_3 surfaces. The FF systems were relaxed until the atomic forces are below $0.01 \text{ eV } \text{\AA}^{-1}$ using the FIRE algorithm. The FF results are in qualitative agreement with the DFT results. Specifically, both PA6 and PAMXD6 exhibit stronger adsorption on the non-terminated surface than on the OH-terminated surface. Moreover, PAMXD6 shows stronger adsorption than PA6 on both surfaces. Therefore, these comparisons confirm that the FF used in this study reasonably captures the interfacial dynamics, supporting the reliability of our atomistic model. We have added the following sentence to page 17 in the revised manuscript and the FF results to Supplementary Fig. 7 of the revised Supplementary Information.

Revision to page 8:

"These adsorption geometries and energies of the PA chains are consistent between the DFT (Supplementary Fig. 6) and classical force fields results used in this study (Supplementary Fig. 7)."

Added to page 17:

"A comparison of adsorption geometries and energies between the DFT and FF validates the reliability of the current atomistic model in describing PA/ Al_2O_3 interactions (Supplementary Fig. 6 and 7)."



Supplementary Figure 7. Assessment of the accuracy of classical force fields used in this study. a) Adsorption configurations of PA6 and PAMXD6 monomers on the OH- and non-terminated Al_2O_3 surface. b) Adsorption energies averaged over 5 different adsorption configurations.

F) Furthermore, to quantify the conformational changes of adsorbed chains a local radius of gyration is used. The results are interesting but there is no information about the anisotropic shape of polymer chains. Other metrics involving the local radius of gyration tensor and the asphericity ratio would be more useful.

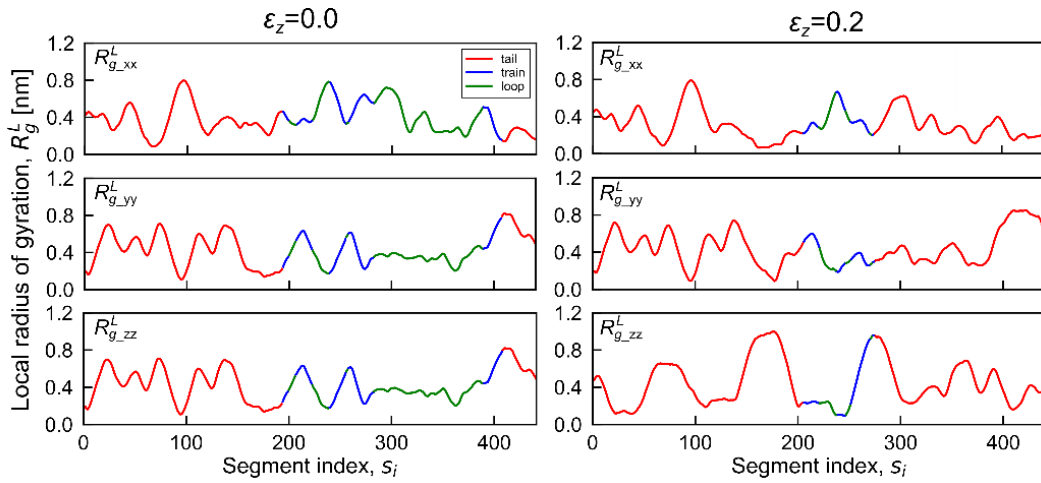
Reply:

We appreciate the reviewer's important comment. We agree that analyzing the anisotropy of polymer conformations would provide important complementary information. We calculated the diagonal components of the local radius of gyration tensor R_g^L and plotted the results as in Fig. 7g. As shown in Supplementary Fig. 10, conformational changes are pronounced in the zz component, particularly in regions where loop-to-trail transitions occur, while variations in the xx and yy components remain relatively small. This trend is further highlighted in Supplementary Fig. 11, which shows the differences in the diagonal components of R_g^L between $\varepsilon_z = 0.0$ and 0.2 . Notably, large anisotropic changes are observed around $s \approx 180$ and 270 , corresponding to boundaries between trains and tails (as shown in Fig. 7g). Due to partial desorption of trains, structural relaxation also occurs in the x axis especially around $s \approx 270$. These results demonstrate that the local radius of gyration tensor proposed in this study can be useful to

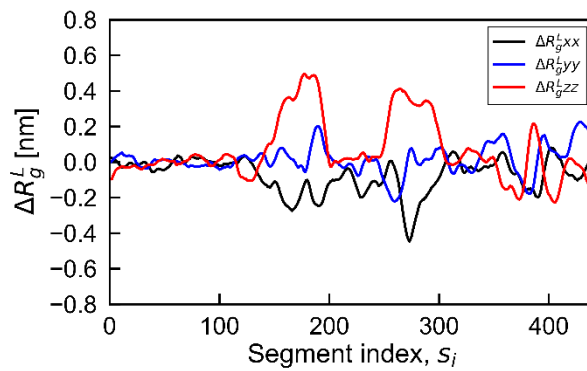
capture the anisotropic conformational dynamics at a segmental scale under mechanical loading. We are planning to fully develop the tensorial formulation of the local radius of gyration and define shape metrics (such as the asphericity ratio, as the reviewer suggested), to further explore the segmental-scale mechanics of adsorbed polymer chains. We have added Supplementary Fig. 10 and 11 to the revised Supplementary Information and the following sentence to page 12 of the revised manuscript.

Added to page 12:

“The anisotropy in local conformational changes was assessed by calculating the diagonal components of the R_g^L tensor (Supplementary Fig. 10 and 11), revealing that conformational deformation occurs predominantly along the tensile direction, particularly near train-to-tail transitions but also in the x axis due to partial desorption and subsequent structural relaxation.”



Supplementary Figure 10. Evolution of the local radius of gyration tensor components $R_g^L(I, s = 30)$ along the chain at $\varepsilon_z = 0.0$ (left) and 0.2 (right) for a representative PAMXD6 chain adsorbed on the OH-terminated surface during tensile deformation.



Supplementary Figure 11. Changes $\Delta R_g^L(I, s = 30)$ in the local radius of gyration tensor components along the chain between $\varepsilon_z = 0.0$ and 0.2 , calculated from the results in Supplementary Fig. 10.

G) Last, but not least, the value of this work would be greatly enhanced by comparing, if possible, the predictions of the CG model with experimental data, if feasible. For example, experimental

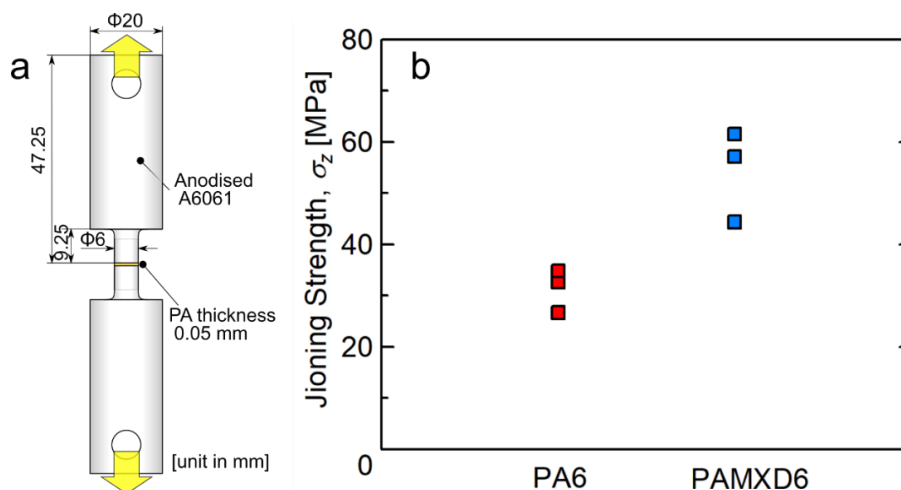
data on interfacial thickness, chain orientation, or mechanical behavior could help validate the atomistic predictions presented in the manuscript.

Reply:

Since no experimental data was available for the joining strength of PAMXD6, we conducted tensile tests for both PA6 and PAMXD6 bonded to anodized aluminum alloy (A6061-T6). The PA pellets were melt-joined to cylindrical, anodized A6061-T6 specimens (Supplementary Fig. 1a), and tensile tests were performed at 25 °C with a tensile speed of 0.5 mm min⁻¹ using a Minebea TG-100kN machine (Supplementary Fig. 1b). The results show that the averaged joining strengths were 29.2 MPa for PA6 and 52.6 MPa for PAMXD6. The experimental results qualitatively support our AA-MD findings, where PAMXD6 exhibits higher interfacial strength than PA6. The quantitative differences in interfacial strength between the simulations and experiments can be attributed to various multiscale factors not captured in our simulations, e.g. surface morphology, impurities, and processing conditions. We have added the following sentence to page 5 in the revised manuscript and Supplementary Fig. 1 to the revised Supplementary Information.

Added to page 5:

“Tensile tests of PA6 and PAMXD6 joined with anodized alumina alloy show that PAMXD6 exhibits a higher average joining strength ($\sigma_z^{\max} = 52.6$ MPa) than PA6 ($\sigma_z^{\max} = 29.2$ MPa), consistent with the trend observed in the AA-MD simulation (Supplementary Fig. 1).”



Supplementary Figure 1. Tensile tests of PA6 and PAMXD6 joined with an anodized aluminum alloy (A6061-T6): a) Tensile specimen geometry and b) joining strength of PA6 (red) and PAMXD6 (blue).

Reviewer #2 (Remarks to the Author):

This manuscript provides a molecular-level understanding of the adsorption phenomena at the polymer/Al₂O₃ interface by introducing segment-scale analysis. The following minor comments are provided for the authors' consideration:

1. "These differences observed in the S–S behavior of..."

The discussion centers around localized deformation and void formation. However, Fig. 3 is based

on displacement, and strictly speaking, displacement from the initial configuration does not directly represent local deformation. Previous studies have addressed similar phenomena using local strain and free volume as indicators. The authors are encouraged to cite and consider the methodology used in the following reference:

<https://doi.org/10.1016/j.commatsci.2023.112333>

Reply:

Thank you for the insightful suggestion. Kawagoe et al. used the Green-Lagrange strain tensor *using* corrected smoothed particle hydrodynamics (SPH) E_{zz}^{SPH} , offering a valuable atomistic perspective to characterize local deformation fields. Following their methodology, We evaluated per-atom strain, and have revised Fig. 3 accordingly in the revised manuscript. We have also added the following sentence to page 6 of the revised manuscript.

Added to page 6:

“To visualize local inhomogeneous deformation near the PA/ Al_2O_3 interface, Green-Lagrange strain tensor using corrected smoothed particle hydrodynamics (SPH) E_{zz}^{SPH} , proposed by Kawagoe and Okabe²⁸, were employed.”

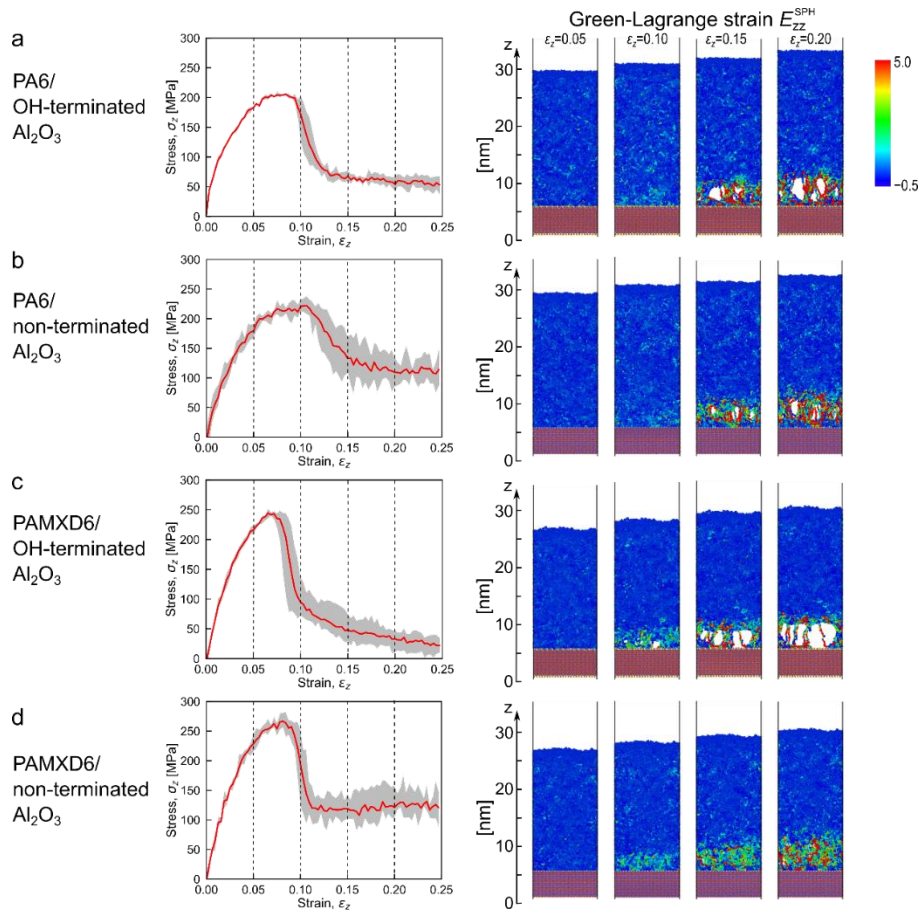


Figure 3. Averaged stress–strain curves (left) and Green-Lagrange strain E_{zz}^{SPH} at selected strain values (right): a) PA6/OH-terminated Al_2O_3 , b) PA6/non-terminated Al_2O_3 , c) PAMXD6/OH-terminated Al_2O_3 , and d) PAMXD6/non-terminated Al_2O_3 joining interface. Dashed vertical lines in the plots indicate the strain values at which the corresponding snapshots were taken. Gray-shaded regions represent the standard deviations over five

independent MD simulations. Each was performed with different initial configurations of amorphous PA models.

2. Regarding the definition of local radius of gyration

It is expected that the local radius of gyration approaches the normal radius of gyration as the segment length s increases. However, in Fig. 7, R_g appears to increase monotonically without saturation. Does this imply that the range of s used is significantly smaller than the full chain length? Please clarify the scale of s in relation to the total chain length.

Reply:

Thank you for pointing this out. In the revised Fig. 1, we have labeled the backbone atoms used to calculate the local radius of gyration R_g^L for both PA6 and PAMXD6. The degrees of polymerization are 52 for PA6 and 36 for PAMXD6, corresponding to maximum segment lengths $s_{\max}$ of 364 and 432, respectively. Therefore, $\langle R_g^L \rangle$ at $s = s_{\max}$ is equivalent to the conventional (global) radius of gyration ($R_g \approx 3$ nm). In Fig. 7b-e, the $\langle R_g^L \rangle$ curves are plotted up to $s = s_{\max}$, and their monotonic increase reflects the scaling behavior of polymer chain conformations. We have clarified this in the revised Fig. 1 and caption.

We believe that the variation of $\langle R_g^L \rangle$ with s and tensile strain effectively captures how local conformational changes evolve into global chain responses, demonstrating its utility in describing segmental-scale mechanical behaviors. In future work, we plan to generalize this scalar quantity to a gyration tensor to characterize anisotropic deformations and better understand the origins of such monotonic behavior.

Added to page 11-12:

“Note that $\langle R_g^L(s) \rangle$ at $s = s_{\max}$ corresponds to the conventional global radius of gyration. The backbone atoms used are shown in Fig. 1; $s_{\max}$ equals 364 for PA6 and 432 for PAMXD6 in our simulations.”

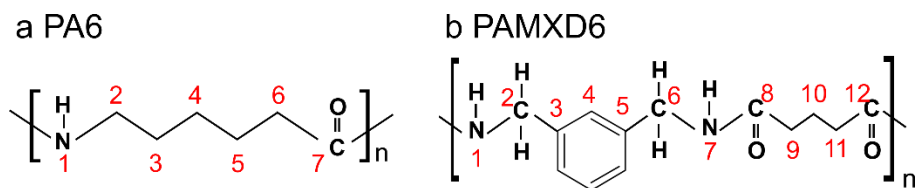


Figure 1. Structural formula of polyamides: a) PA6 and b) PAMXD6. Backbone atoms used for the calculation of the local radius of gyration (Fig. 7) are indicated by numbers. The total numbers of backbone atoms are 364 for PA6 and 432 for PAMXD6 in our simulations.

3. On Fig. 7g

The figure is somewhat difficult to interpret and would benefit from improvement. Given that the definition of R_g captures local structural features, the absolute values are expected to show only small changes, making absolute comparisons less informative. Rather than emphasizing the magnitude of R_g , it would be more meaningful to clearly indicate how each chain segment—classified as train, loop, or tail—evolves during deformation. The current visualization does not readily convey this transition.

Reply:

We apologize for the lack of clarity in the original Fig. 7g. We agree with the reviewer that absolute values of $R_g^L(s)$ are not particularly informative. Our intent in Fig. 7g is to illustrate how local conformational changes correlate with transitions between train, loop, and tail segments, in conjunction with the sequential snapshots. In particular, the change $\Delta R_g^L(s)$ with strain highlights regions of stress release and structural relaxation, which tend to coincide with transitions between these segmental states. In the revised Fig. 7g, we have separated the $R_g^L(s)$ plots at different strain levels, eliminating the overlap that obscured the trends in the original one. Moreover, we have modified the snapshots to explicitly highlight the region ($s = 270 - 410$) where loop-to-tail transitions occur. To provide a clear, step-by-step picture of molecular desorption under tensile strain, we additionally included four sequential snapshots and added black and orange arrows to indicate the initial boundaries of a train segment, which later undergoes transitions into loop and tail segments. These revised visualization clearly illustrate how segmental transitions evolve during tensile deformation. We hope that the revised Fig. 7g addresses the reviewer's concern and effectively conveys the underlying conformational dynamics.

Added to page 12:

“Black and orange arrows in the sequential snapshots and R_g^L curves indicate the initial boundaries of a train segment $\varepsilon_z = 0.0$, which later undergo transitions into loop and tail segments. These snapshots demonstrate that tensile strain induces gradual desorption of train segments and local structural relaxation leading to the formation of new train segments (see the snapshot at $\varepsilon_z = 0.09375$ in the top panel of Fig. 7g).”

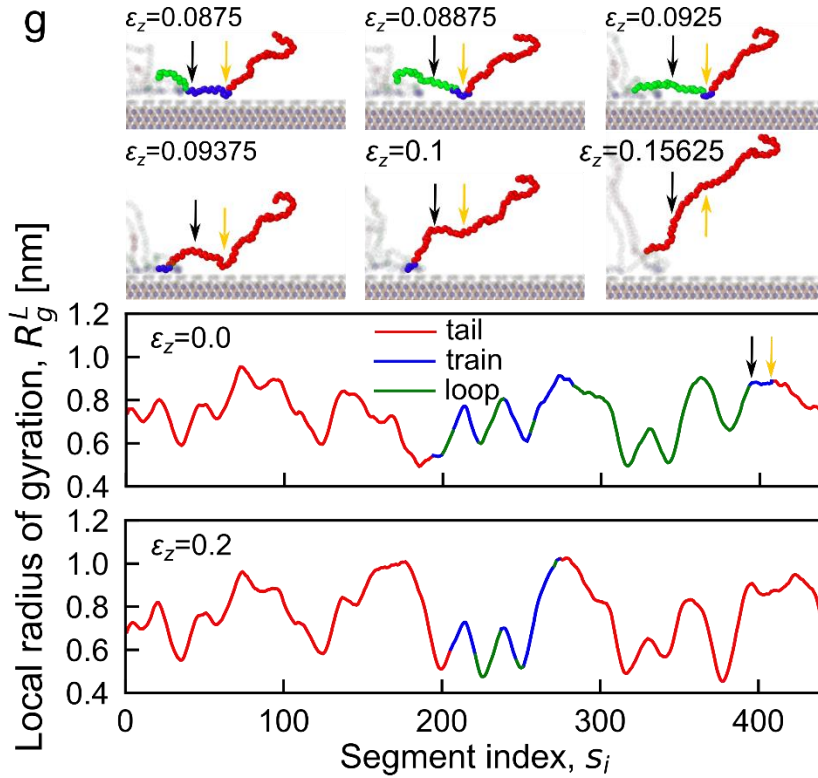


Figure 7g. Evolution of the conformation (top) and the local radius of gyration $R_g^L(I, s = 30)$

at $\varepsilon_z = 0.0$ (middle) and 0.2 (bottom) for a representative PAMXD6 chain adsorbed on the OH-terminated surface during tensile deformation. Black and orange arrows indicate the initial boundaries of a train segment at $\varepsilon_z = 0.0$, which later undergoes transitions into loop and tail segments.

4. Regarding MD boundary conditions

The manuscript states that periodic boundary conditions are applied in all three spatial directions. For slab-type systems like this, it is well known that spurious dipole interactions may arise due to artificial periodicity in the z-direction. In such cases, dipole corrections (e.g., `kspace_modify_slab` in LAMMPS) are often applied. Did the authors implement this correction? If not, there may be non-negligible artifacts from periodic images. Please consider the following reference for more details: <https://doi.org/10.1063/1.479595>

Reply:

We appreciate the reviewer's insightful comment. We employed three-dimensional periodic boundary conditions with a sufficiently thick vacuum layer. As shown in Supplementary Fig. 14b, the Al_2O_3 slab has a thickness of 24 nm, while the thickness of the vacuum layer is 75 nm, i.e. more than three times thicker than the slab itself. Therefore, slab-slab interactions are negligibly small. We have added the following sentence to page 18 of the revised manuscript.

Added to page 18:

"A vacuum region of 75 nm was introduced along the z axis, more than three times thicker than the Al_2O_3 slab, which effectively suppresses slab-slab spurious interactions."

Reviewer #3 (Remarks to the Author):

This manuscript compares the adsorption behavior and high-strain conformational evolution of the linear aliphatic PA6 versus the aromatic PMXD6 on both OH-terminated and non-terminated $\alpha\text{-Al}_2\text{O}_3(0001)$ surfaces. Through all-atom MD simulations, three key conformational modes are identified, and DFT adsorption energy calculations offer the physicochemical basis for the desorption mechanisms observed in MD. The manuscript is logically organized with sound analysis. Some suggestions are provided below:

1. Please explicitly state that Δz represents the absolute value of the coordinate difference.

Reply:

We thank the reviewer for the constructive comments. We agree that the previous definition of Δz in Fig. 3 was ambiguous and could lead to confusion. To address this issue, we have revised Fig. 3 to use the Green-Lagrange strain tensor E_{zz}^{SPH} based on corrected smoothed particle hydrodynamics (SPH). This strain tensor is widely used to characterize inhomogeneous strain fields for heterogeneous systems with an interface. We believe it provides a more accurate representation of localized deformation than the simple coordinate difference Δz . We have added the following sentence to page 6 of the revised manuscript and page 3 of the revised Supplementary Information.

Added to page 6:

“To visualize local inhomogeneous deformation near the PA/Al₂O₃ interface, Green-Lagrange strain tensor using corrected smoothed particle hydrodynamics (SPH) E_{zz}^{SPH} , proposed by Kawagoe and Okabe²⁸, were employed.”

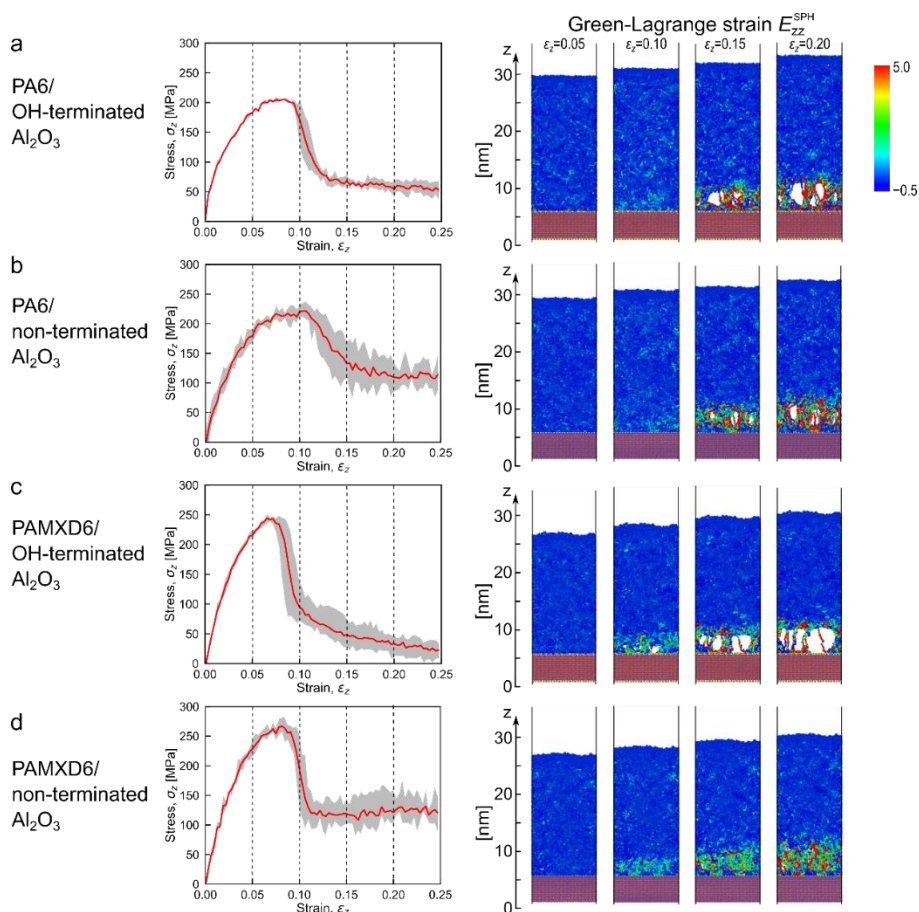


Figure 3. Averaged stress–strain curves (left) and Green-Lagrange strain E_{zz}^{SPH} at selected strain values (right): a) PA6/OH-terminated Al₂O₃, b) PA6/non-terminated Al₂O₃, c) PAMXD6/OH-terminated Al₂O₃, and d) PAMXD6/non-terminated Al₂O₃ joining interface. Dashed vertical lines in the plots indicate the strain values at which the corresponding snapshots were taken. Gray-shaded regions represent the standard deviations over five independent MD simulations. Each was performed with different initial configurations of amorphous PA models.

2. Cite the original experimental and/or simulation studies that established 0.45 nm as the adsorption cutoff to justify its use.

Reply:

The cutoff distance of 0.45 nm was determined based on the thickness of the first adsorption layer observed in the polymer density profile (Fig. 5). The thickness is defined as the distance from the Al₂O₃ surface to the first minimum (valley) between the first and second peaks, as in previous studies (e.g. J. Phys. Chem. B 2022, 126, 7429-7444). Other studies have used comparable cutoff values, 0.4 nm in Macromolecules 2023, 56, 6552-6564, and 0.55 nm in Nano Lett. 2024, 24, 148-155. We added this justification and corresponding references to page 10 of

the revised manuscript.

Added to page 10:

“The cutoff of 0.45 nm was chosen based on the thickness of the first adsorption layer observed in the density profiles in Fig. 5, defined as the distance from the Al_2O_3 surface to the first minimum between the first and second peaks²⁰.”

3. Explain how the uniaxial strain rate of $6.4 \times 10^{-6} \text{ fs}^{-1}$ was determined. Provide the theoretical rationale or reference prior work.

Reply:

Thank you for the helpful comment. The tensile displacement rate of $5.0 \times 10^{-6} \text{ nm fs}^{-1}$ used in our simulations is comparable to $2.0 \times 10^{-6} \text{ nm fs}^{-1}$ used by Hagita et al. (Langmuir 2023, 39, 7063-7078) and much slower than $2.0 \times 10^{-3} \text{ nm fs}^{-1}$ by Liu et al. (Polymer Composites. 2025, 1–14). To assess the influence of strain rate on interfacial mechanics, we performed additional simulations of the PA6/non-terminated Al_2O_3 system at two displacement rates of 2.5×10^{-6} and $1.0 \times 10^{-5} \text{ nm fs}^{-1}$. Figure R2 shows comparisons of the resulting stress-strain curves and Green-Lagrange strain E_{zz}^{SPH} . The stress-strain behavior, including the maximum tensile stress, is nearly identical across all three rates, with variations within the standard deviation over three independent MD trajectories. The E_{zz}^{SPH} distributions also exhibit similar trends in nano-void formation and local deformation near the interface, although the highest rate of $5.0 \times 10^{-5} \text{ nm fs}^{-1}$ shows slightly reduced relaxation, as evidenced by smaller regions of high E_{zz}^{SPH} . These results indicate that the strain rate of $5.0 \times 10^{-6} \text{ nm fs}^{-1}$ is sufficiently slow to capture the essential deformation mechanisms. We have added the results at different strain rates to Supplementary Fig. 15 of the revised Supplementary Information and this brief discussion to page 18 of the revised manuscript.

Added to page 18:

“To ensure the robustness of our AA-MD results, additional simulations were conducted at two different displacement rates of 2.5×10^{-6} and $1.0 \times 10^{-5} \text{ nm fs}^{-1}$ (Supplementary Fig. 15). The maximum tensile stress and local deformation patterns were largely independent of strain rate, confirming that the chosen rate of $5.0 \times 10^{-6} \text{ nm fs}^{-1}$ provides representative deformation behavior.”

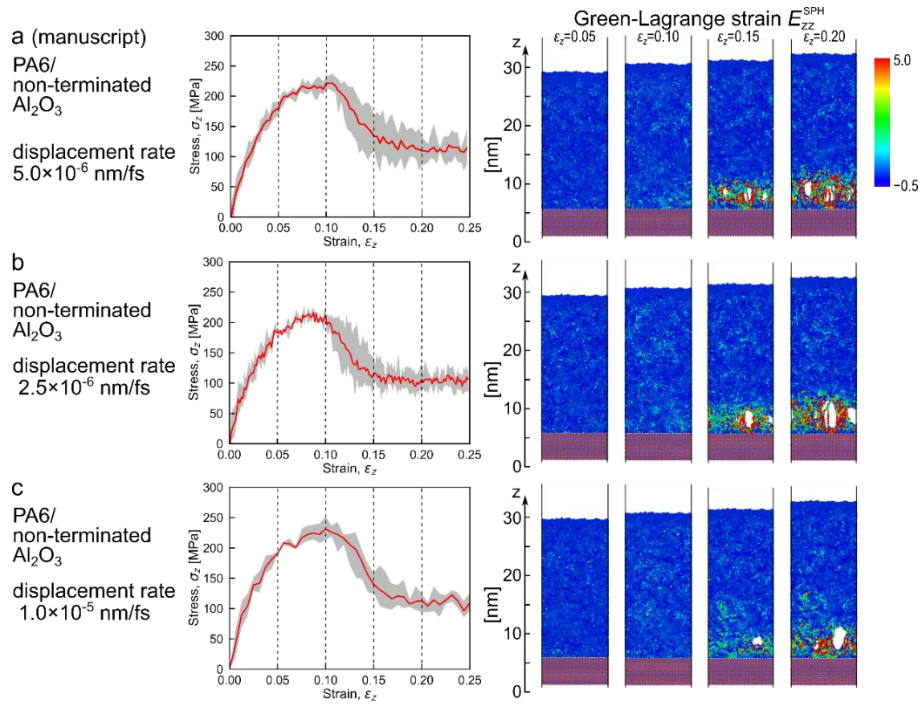


Figure R2. Stress-strain curves and spatial distributions of Green-Lagrange strain E_{zz}^{SPH} of PA6/non-terminated models at three different tensile displacement rates: a) 5.0×10^{-6} , b) 2.5×10^{-6} , and c) 1.0×10^{-5} nm fs $^{-1}$.

4. Because PA6 and PMXD6 contain different numbers of backbone atoms per monomer, it might be more reasonable to normalize the average segment length $\langle s \rangle$.

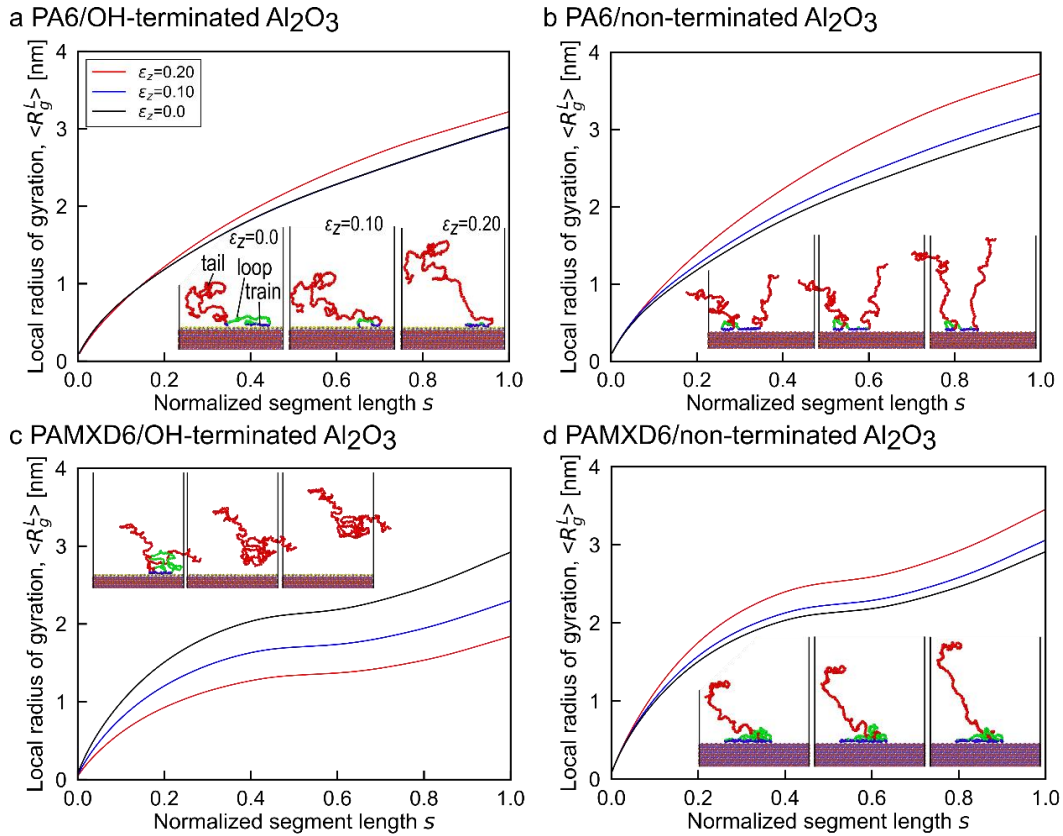
Reply:

We are grateful for this insightful suggestion. We have additionally plotted the local radius of gyration $\langle R_g^L \rangle$ as a function of the normalized segment length $s/s_{\max}$, where $s_{\max}$ denotes the full segment length of each polymer chain (Supplementary Fig. 9). This normalized representation allows us to capture the relative scale of conformational chains with each chain. We have added Supplementary Fig. 9 to the revised Supplementary Information and the following sentences to page 12 of the revised manuscript.

At the same time, we emphasize that the absolute segmental length s remains a meaningful physical quantity, especially when discussing characteristic segmental scale of conformational deformation in adsorbed chains. Therefore, in the main text we retain the original plot as a function of s , while the normalized plots are provided in the revised Supplementary Information for reference. We also plan to develop a follow-up study that further explores the utility of $\langle R_g^L \rangle$ and extends this scalar measure to a gyration tensor for capturing anisotropic conformational changes.

Added to page 12:

“Plots of $\langle R_g^L \rangle$ as a function of normalized segment length $s/s_{\max}$ for PA6 and PAMXD6 are provided in Supplementary Fig. 9. This representation helps compare the relative scale of structural deformation between PA6 and PAMXD6.”



Supplementary Figure 9. Local radius of gyration $\langle R_g^L(s) \rangle$ as a function of the normalized segment length $s/s_{\max}$, where $s_{\max}$ denotes the full segment length of each polymer chain: a) PA6/OH-terminated Al₂O₃, b) PA6/non-terminated Al₂O₃, c) PAMXD6/OH-terminated Al₂O₃, and d) PAMXD6/non-terminated Al₂O₃.

5. To substantiate claims like “the oxygen atoms are oriented toward the surface,” it would be necessary to include a quantitative metric of amide orientation, such as the angle between the C=O bond vector and the surface normal.

Reply:

Thank you for the important suggestion. To quantitatively assess the orientation of amide groups, we calculated the local orientational order parameter P_2 based on the angle θ between the C=O bond vector and z axis. The order parameter P_2 is defined as:

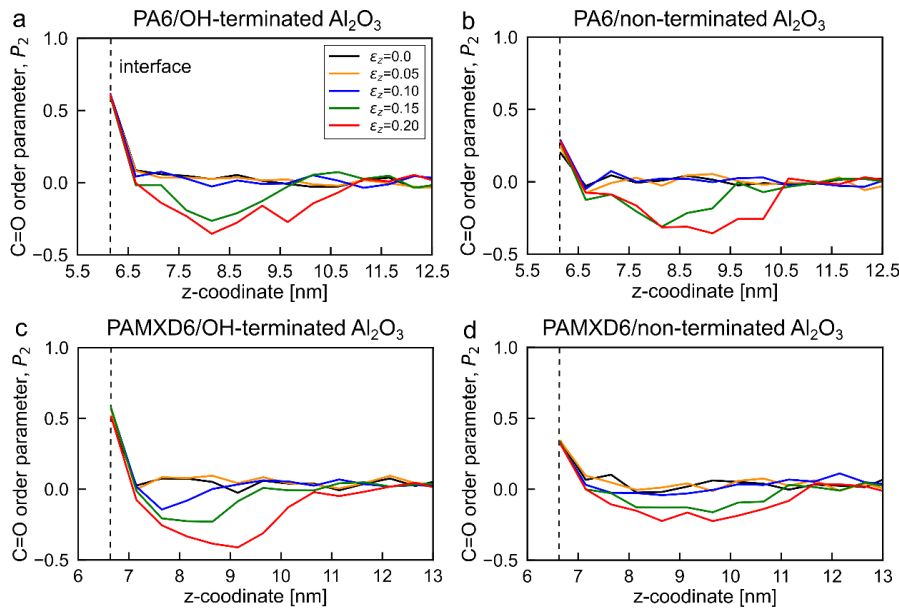
$$P_2 = \left\langle \frac{3\cos^2\theta - 1}{2} \right\rangle,$$

where the brackets indicate averaging over all C=O bonds within a bin width of 0.5 nm. A value of $P_2 = 1$ corresponds to full alignment along the z axis, whereas $P_2 = -0.5$ indicates perfect perpendicular alignment. $P_2 = 0$ denotes random orientation. Supplementary Figure 5 shows the depth profiles of P_2 for PA6 and PAMXD6 under tensile deformation. On the OH-terminated surface (Supplementary Fig. 5a and c), both PA6 and PAMXD6 exhibit strong interfacial alignment ($P_2 \approx 0.6$), indicating that C=O bonds are oriented along the z axis. As deformation proceeds, P_2 decreases rapidly and approaches 0.0, reflecting disorder in the orientation of C=O bonds. After yielding, P_2 at the interface remains relatively constant, while P_2 in the region ~ 4 nm from the interface P_2 decreases to about -0.3. This suggests that the C=O bonds reorient perpendicular to the z axis in regions where chain stretching and nanovoid formation occur (see

also Fig. 3). Similar trends are observed on the non-terminated surface (Supplementary Fig. 5b and d), although the initial interfacial alignment is weaker ($P_2 \approx 0.3$). These analyses confirm that oxygen atoms in amide groups preferentially orient toward the surface, supporting our original statement. We added Supplementary Fig. 5 to the revised Supplementary information and the following description to page 8 of the revised manuscript.

Added to page 8:

“This indicates that the O atoms are oriented toward the Al_2O_3 surface (Fig. 5e), **as supported quantitatively by the local orientational order parameter analysis (Supplementary Fig. 5).**”



Supplementary Figure 5. Evolution of the depth profiles of the local orientational order parameter P_2 : **a)** PA6/OH-terminated Al_2O_3 , **b)** PA6/non-terminated Al_2O_3 , **c)** PAMXD6/OH-terminated Al_2O_3 , and **d)** PAMXD6/non-terminated Al_2O_3 .

6. In Fig. 7g, assign distinct colors so that the $\epsilon_z = 0.0$ and $\epsilon_z = 0.2$ curves can be easily distinguished, and ensure train/loop/tail each has their unique color for visual purpose (the current plot uses red for both $\epsilon_z = 0.2$ and “tail,” which should be corrected).

Reply:

We apologize for the confusion in the original Fig. 7g. In the revised version, we have substantially improved clarity by separating the $R_g^L(s)$ plots at different strain levels (as also noted in our reply to Reviewer 2), thereby eliminating overlap of the two curves. Moreover, we modified snapshots to clearly illustrate how train segments desorb under tensile strain. These changes allowed us to assign distinct and consistent colors to each segment type, i.e. train, loop, and tail, to avoid ambiguity. The revised figure has been included in the revised manuscript.

Added to page 12:

“Black and orange arrows in the sequential snapshots and R_g^L curves indicate the initial boundaries of a train segment $\epsilon_z = 0.0$, which later undergo transitions into loop and tail segments. These snapshots demonstrate that tensile strain induces gradual desorption of train

segments and local structural relaxation leading to the formation of new train segments (see the snapshot at $\varepsilon_z = 0.09375$ in the top panel of Fig. 7g)."

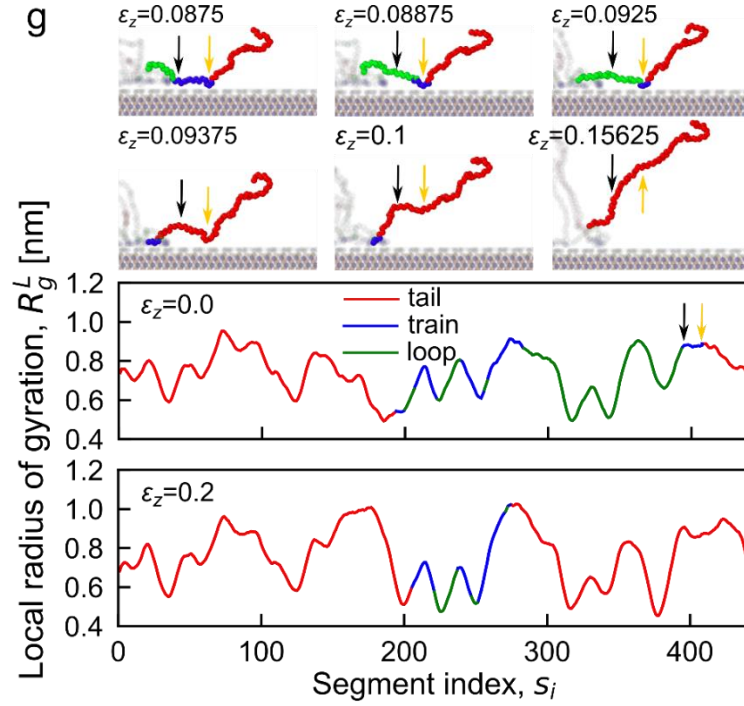


Figure 7g. Evolution of the conformation (top) and the local radius of gyration $R_g^L(I, s = 30)$ at $\varepsilon_z = 0.0$ (middle) and 0.2 (bottom) for a representative PAMXD6 chain adsorbed on the OH-terminated surface during tensile deformation. Black and orange arrows indicate the initial boundaries of a train segment at $\varepsilon_z = 0.0$, which later undergoes transitions into loop and tail segments.

Point-by-point response to the reviewers' comments

We thank all three reviewers for their careful reading of the revised manuscript and Supplementary Information, and for recommending the paper for publication. We have revised the manuscript in accordance with the constructive comments from Reviewer 1. Please see our replies in black below.

Reviewer #1:

I am glad to see that Authors considered most of my comments in the revised draft. Nevertheless, I still have major concerns regarding its suitability for publication in a broad high impact factor journal such as Nature Communications.

My primary concern remains the novelty of the presented data. For instance, Authors claim that “we would like to emphasize that the key novelty of our study lies in the introduction of the local radius of gyration $\langle R_g^L \rangle$ as a segmental-scale structural descriptor”. This claim is not accurate as the structure of polymer chains at interfaces via several metrics, including local radius of gyrations, has been extensively investigated over the past decades within the simulation community.

Reply:

Thank you very much for your important comment. We fully agree that the interfacial structures between polymers and inorganic surfaces have been characterized using various structural metrics. However, we respectfully disagree that the local radius of gyration has been “extensively” investigated. To the best of our knowledge, only a couple of studies have explicitly used the term “local radius of gyration” R_g^L in the context of polymer simulations: RSC Adv. (2019), 9, 33549; J. Chem. Phys. (2008), 128, 144903; ACS Macro Lett. (2020), 9(10), 1483–1488. In these works, R_g^L was defined simply as the radius of gyration R_g calculated over the particles located within the interfacial region near the substrate. Therefore, “local” literally means a summation over particles in a local space, e.g. $R_g^{L^2} = \frac{1}{M} \sum_{i \in \text{interface region}} m_i (r_i - r_{\text{cm}})^2$. In contrast, in our study, we define R_g^L by introducing a segmental length s along the molecular chain and then computing R_g for such chain segments. This approach allows us to capture “scale-dependent” conformational behavior within a polymer chain, which cannot be resolved by the “position-dependent” quantity in previous works. Moreover, we demonstrate that this descriptor provides new insights into (i) three distinct desorption modes during tensile deformation and (ii) the different conformational responses of four types of polymer/metal interfaces with distinct chemical functionalities. We have cited these papers and emphasized this conceptual novelty in the Introduction of the revised manuscript.

Added to page 11:

“ R_g^L has been introduced in previous research papers^{29–31}, where it was defined as the radius of gyration R_g calculated over the particles located within the interfacial region near the substrate. By contrast, our definition of R_g^L allows us to capture scale-dependent local conformational behavior within a polymer chain, which cannot be resolved by the conventional position-dependent descriptor used in the previous works.”

Similarly, the Authors argue that the use of all-atom is essential to capture interfacial behavior, stating that “our all-atom MD study highlights the critical role of chemical functionalities in both PA chains and Al₂O₃ surfaces, which are absent in typical coarse-grained” While this point is valid, it is a bit generic since the necessity of atomistic resolution for capturing interfacial phenomena has already been well established in the literature.

Reply:

We appreciate this critical comment. Indeed, the adsorption dynamics of polymer chains on metal surfaces have been studied using all-atom molecular dynamics (MD) simulations: e.g. ACS Appl. Polym. Mater. (2022), 4, 6038–6046; Langmuir (2016), 32, 4450–4463. Our intention was not to claim the necessity of atomistic resolution as a general novelty, but rather to emphasize the specific advantage of the fully atomistic representation in the present context of polymer-metal joint interfaces under tensile deformation. In particular, our simulations reveal that PA chains physisorb on Al₂O₃ surfaces via both the oxygen atoms of the amide groups and hydrocarbon units, and that this adsorption can persist even at large strains. Moreover, we show that the atomistic details of both the polymer and the surface chemistry critically determine the persistency of adsorption, leading to distinct desorption modes and interfacial strengths. These insights go beyond a generic statement on atomistic necessity, as they directly link chemistry-specific interfacial interactions with mechanical performance, thereby contributing to the atomistic understanding and design of durable multi-material hybrid components. We have added the following sentence to the revised manuscript.

Added to page 16:

“In particular, this study demonstrates how the amide groups and hydrocarbon units in PA chains affect their adsorption on Al₂O₃ surfaces and the persistence of this adsorption under large tensile strains, and how these effects determine the mechanical strength of PA/Al₂O₃ interfaces.”

Below I provide additional, more specific technical comments:

1) Equilibration of polymeric systems (Previous comment C): Authors add a new section (S11, Figure 13) discussing the relaxation state of the amorphous structure. As expected, there is not any relaxation at 300K since the system is in glassy state, so there is no point in presenting the end-to-end vector autocorrelation function that remains constant at one during time.

The critical question is whether the systems are well relaxed at higher temperatures. The internal distance data (Fig. 13b) do not display the Gaussian statistics typical of well-relaxed conformations, which indicates insufficient equilibration. This could have unclear effects on the predicted mechanical properties of the systems. Given the additional challenges of equilibrating interfacial conformations, it is even more questionable whether the interfacial layer is adequately relaxed, i.e., i.e. that its structure is not strongly dependent on the history of the system, such as the cooling rate and the initial, rather unrealistic high, temperature of 1000K. The above issues can be investigated by different cooling protocols, involving (much) longer MD simulations and statistics over multiple uncorrelated configurations.

Reply:

We sincerely appreciate the reviewer’s constructive comments. **First**, we would like to emphasize that our study adopts essentially the same relaxation protocol as previous all-atom MD works,

following the widely accepted sequence of random packing, densification, cooling, and equilibration (see Table R1 below). **Second**, the purpose of the 1000 K equilibration step is to accelerate conformation rearrangements and shorten the time required to approach Gaussian statistics. **Third**, as shown in Fig. 3, the stress–strain curves obtained from five independent initial configurations converge to nearly identical values and are consistent qualitatively with additional experimental and DFT results (Supplementary Fig. 1 and 6, respectively). This confirms that our preparation protocol effectively removes the dependence of the non-equilibrium interfacial dynamics on the initial configurations and is sufficient to achieve the objectives of this study. Furthermore, the statistical robustness of our models is supported by the reproducibility of local conformational dynamics, i.e. distinct desorption modes (Fig. 8) governed by the chemical characteristics of polymer chains and Al_2O_3 surfaces.

We acknowledge that achieving complete thermal equilibration of polymers is practically unfeasible in fully atomistic simulations. Typical simulations times in previous all-atom studies are limited to 1–10 ns (e.g., *Nat. Commun.* (2024), 15, 1898; *ACS Appl. Polym. Mater.* (2022), 4, 6038–6046; *Macromolecules* (2024), 57, 3949–3966), in contrast to μs timescales accessible by CG simulations. Due to the enormous computational cost of all-atom MD, hundreds-of-ns-long equilibration runs remain beyond reach even on state-of-the-art supercomputers, unless much smaller systems are used. Nevertheless, such previous studies successfully modeled the interfacial dynamics of polymers on metals and their mechanical responses, as is also the case in the present study. As summarized in Table R1, our preparation protocol follows the general strategy of previous studies but with substantial extensions. For example, Kawagoe et al. (*Polymer* (2019), 180, 121721) investigated a 76,800-atom system with only 50 ps equilibration at 1000 K, a short 0.2 ns cooling, and a 5 ns NPT run. By contrast, our systems are considerably larger (198,000 atoms), and employed (i) a much longer equilibration at 1000 K (10 ns vs. 0.05 ns in Kawagoe et al.), (ii) slower cooling from 1000 K to 300 K over 0.7 ns instead of 0.2 ns, and (iii) a 10 ns equilibration at 300 K. Other studies used even smaller systems and shorter equilibration—for example, Chantawansri et al. (*Polymer* (2015), 81, 50–61) with 17,400 atoms and 7 ns at 700 K, Liu et al. (*Macromolecules* (2024), 57, 3949–3966) with $\sim 15,000$ atoms and 12 ns cooling, or Yamamoto et al. (*ACS Appl. Polym. Mater.* (2020), 2, 1474–1481) with $\sim 31,000$ atoms and 1 ns equilibration at 296 K. Importantly, compared with these prior studies, our procedure incorporates several improvements: (i) longer high-temperature relaxation (0.05 ns vs. 10 ns in our case) and slower cooling (0.2 ns vs. 0.7 ns), (ii) gradual densification using smooth-wall potentials instead of instantaneous cell shrinkage, and (iii) extended equilibration with detailed structural analyses. These steps were specifically introduced to ensure that our amorphous PA6 and PAMXD6 models are well relaxed within the limits of computational feasibility.

Furthermore, to address the reviewer’s concern regarding the cooling protocol, as already shown in Section 3 of the revised SI, we prepared another PA6 sample with a lower quench rate of 0.1 K ps^{-1} (compared to 1 K ps^{-1} used in the main text), followed by tensile simulations. The results show that both the maximum tensile stress and interfacial responses, including local inhomogeneous displacements after yielding, remain nearly identical. This comparison demonstrates that, within the computationally feasible range, the interfacial structure and the mechanical behavior are robust against reasonable variations in the cooling protocol.

Table R1. Comparison of preparation protocols in this study and the references.

	Step			
	(1) Initial configuration	(2) High temperature NPT equilibration	(3) Cooling	(4) 300K NPT equilibration
Present study (PA6/PAMXD6 model)	Random packing. The number of atoms is 198,000 .	10 ns at 1000 K , 1 atm	1000 K → 300 K at a rate of $1.0 \times 10^{-3} \text{ K fs}^{-1}$, corresponding to 0.7 ns	10 ns at 300 K , 1 atm
Kawagoe et al., Polymer (2019), 180, 121721.	Random packing. The number of atoms is 76,800 .	50 ps at 1000 K , 1 atm	1000 K → 300 K during 200 ps	5 ns at 300 K , 1 atm
Chantawansri et al., Polymer, (2015), 81, 50–61.	Random packing. The number of atoms is 17,400 .	7 ns at 700 K , 1 atm	700 K → 100 K during 60 ns . (for calculating T _g)	—
Liu et al., Macromolecules (2024), 57, 3949–3966.	Random packing. The number of atoms is 15,000 .	10 ns at 700 K , 1 atm	1000 K → 300 K during 12 ns	10 ns at 300 K , 1 atm
Kuramochi et al., J. Phys. Chem. B (2009), 113, 15181–15188.	Micelle. The number of atoms is 147,035 .	7 ns at 298.15 K . (for calculating micelle structure change)	—	—
Yamamoto et al., ACS Appl. Polym. Mater. (2020), 2, 1474–1481.	Random packing. The number of atoms is 31,050 .	1 ns at 296 K , 1 atm . (for curing epoxy)	—	—

During the 1000 K equilibration (Step 2), the molecular chains of PA6 and PAMXD6 undergo substantial conformational rearrangements. This relaxation leads to a nearly linear $\langle R^2 \rangle - \Delta$ relation at large Δ , consistent with Gaussian statistics, as shown in Fig. R1a and b. This is further confirmed by the internal distance histograms in Fig. R2. In particular, the $\langle R^2 \rangle - \Delta$ curves display a clear linear regime for Δ above several hundred backbone units, indicating that the chain conformations in the melt approach ideal Gaussian coil behavior and thereby confirming that the segmental conformations are already well equilibrated at 1000 K. It is worth noting, however, that PAMXD6 does not show perfect $\langle R^2 \rangle - \Delta$ linearity since the aromatic rings impose local stiffness and conformational constraints. Moreover, at 300 K, the formation of intermolecular hydrogen-bond networks between amide groups perturbs the random-coil statistics (Fig. R1c), consistent with the previous observations for PA6 (*Macromolecules* (2025), 58, 424–438).

Therefore, the observed deviations mainly reflect intrinsic chemical features of the polymer backbones rather than insufficient equilibration. In summary, while longer simulations would of course be desirable for achieving better relaxation, our all-atom models yield consistent structural and mechanical responses, which supports the validity and robustness of our conclusions. We have added a brief note on the relaxation states of our models to the revised manuscript and Fig. R1 and 2 to the revised SI (Supplementary Fig. 15 and 16, respectively).

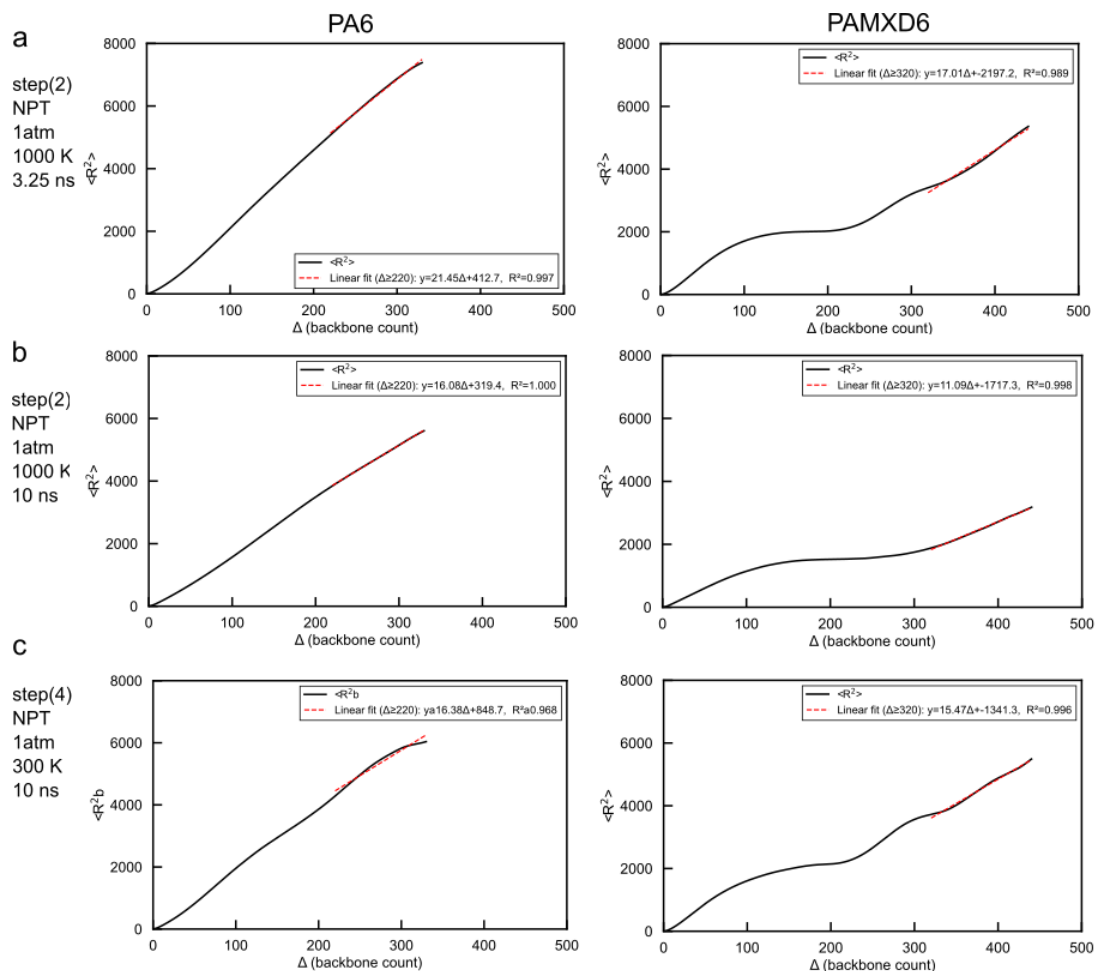


Figure R1. Relaxation behavior and chain statistics of amorphous PA6 (left panels) and PAMXD6 (right panels). Mean-squared internal distances $\langle R^2 \rangle$ as a function of backbone count Δ at 1000 K after **a)** 3.25 and **b)** 10 ns. Linear fits for large Δ ($\Delta \geq 220$ for PA6 and 320 for PAMXD6) demonstrate that chain conformations approach Gaussian statistics in the melt. PAMXD6 does not show perfect $\langle R^2 \rangle$ - Δ linearity at 300 K since the aromatic rings impose local stiffness and conformational constraints. **c)** $\langle R^2 \rangle$ - Δ relations at 300 K after 10 ns. The formation of intermolecular hydrogen-bond networks between amide groups perturbs the random-coil statistics at large Δ .

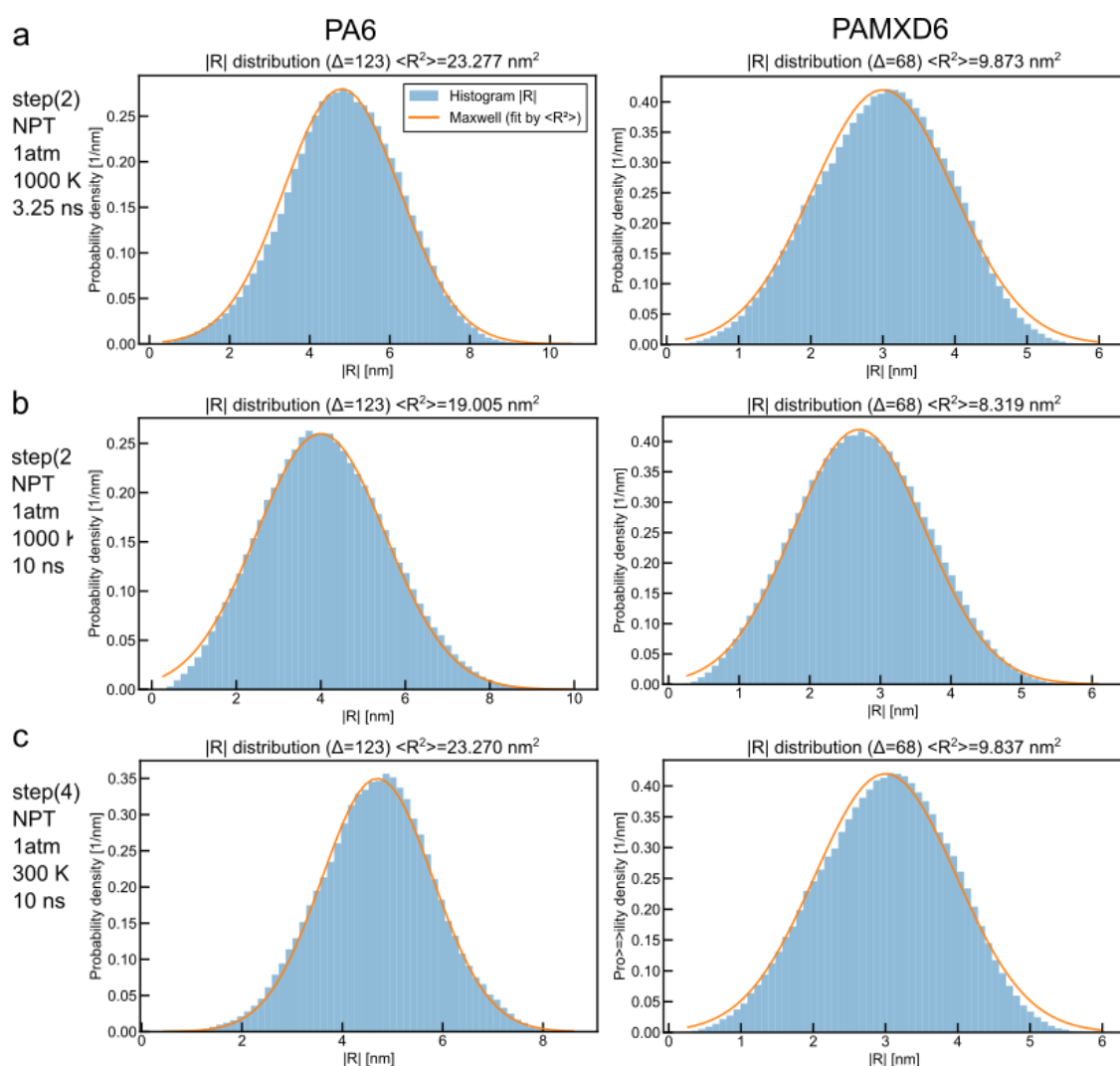


Figure R2. Probability distributions of the internal distance $|R|$ for amorphous PA6 ($\Delta = 123$) and PAMXD6 ($\Delta = 68$): a) after NPT equilibration at 1000 K (3.25 ns), b) after NPT equilibration at 1000 K (10 ns), and c) after NPT equilibration at 300 K (10 ns). At 1000 K, the distributions are well described by Gaussian statistics and remain unchanged between 3.25 and 10 ns, indicating equilibration of segmental conformations.

Added to page 19:

“In particular, mean-squared internal distances $\langle R^2 \rangle$ as a function of backbone atoms Δ for both PA6 and PAMXD6 samples after thermal equilibration at 1000 K exhibit a clear linear regime for long distances ($\Delta > 200$), as shown in Supplementary Fig. 15a and b. PAMXD6 does not show perfect $\langle R^2 \rangle$ – Δ linearity for short distances since the aromatic rings impose local stiffness and conformational constraints. The internal distance distributions are well described by Maxwell-Boltzmann statistics (Supplementary Fig. 16). These results indicate that the chain conformations in the melt approach ideal Gaussian coil behavior and that the segmental conformations are well equilibrated at 1000 K. After quenching to 300 K, the formation of intermolecular hydrogen-bond networks between amide groups perturbs the random-coil statistics (Supplementary Fig. 15c), consistent with the previous observations for PA6⁴³. The observed deviations therefore reflect intrinsic chemical features of the polymer backbones rather than insufficient equilibration.”

Added to page 19:

“Although typical equilibration times in previous all-atom large-scale MD simulations^{44–48} are limited to 1–10 ns, these studies successfully captured the conformational dynamics of polymers on metals and their mechanical properties, as is also the case in the present study. Importantly, compared with these prior studies, our protocol incorporates several improvements: (i) longer high-temperature relaxation and slower cooling, (ii) gradual densification using smooth-wall potentials instead of instantaneous cell shrinkage, and (iii) extended equilibration with detailed structural analyses. These steps were specifically introduced to ensure that our amorphous PA6 and PAMXD6 models are well relaxed within the limits of computational feasibility. The robustness of our models was further confirmed by the convergence of stress-strain curves for five independent trajectories as well as their consistency with experimental and DFT results (Supplementary Fig. 1 and 6, respectively).”

2) DFT calculations and validation of AA FFs (Section S6): Authors present in Supplementary Figures 6 and 7 results related to the “Adsorption geometries and energies of PA monomers on the OH- and non-terminated Al₂O₃ surface using DFT and MD calculations”. First, it is not clear how we can compare adsorption energies (and geometries) at zero temperature (DFT data) with data from MD simulations which include entropic contributions and are closer to free energies of adsorption. Second, the reported values are only qualitatively similar and quantitatively differ substantially. This strongly suggests that the force field is at best qualitatively adequate and does not justify the claim that “the FF used in this study reasonably captures the interfacial dynamics, supporting the reliability of our atomistic model.”

Reply:

We apologize for the confusion. The FF adsorption energies were not calculated from finite-temperature trajectories, but were obtained using the same structural optimization protocol as the DFT calculations, i.e. FIRE algorithm with an optimization criterion of 0.01 eV/Å. We realized that this was only mentioned in the rebuttal letter and not in the manuscript. We have now clarified this in the revised manuscript. Entropic effects are negligible, and thus the comparison with DFT calculations is valid.

Secondly, regarding the quantitative agreement, the present Amber+CLAYFF framework reproduces the averaged adsorption energies of PA monomers on Al₂O₃ surfaces with good accuracy. The deviations from GGA-PBE-D3 results are about 0.1–0.2 eV for PA6 and 0.2–0.3 eV for PAMXD6. More importantly, almost all FF adsorption energies fall within the error bars of the DFT calculations. Such deviations are well within the intrinsic accuracy limits of density functionals. It is well documented that for organic molecules, typical errors of bond formation energies and adsorption energies on metal surfaces relative to experimental data are ~0.3 eV depending on the functional used such as PBE and B3LYP and the empirical dispersion potentials such as TS and D3 [e.g. Proc. Natl. Acad. Sci. U.S.A. (2011), 108, 937-943; Org. Lett. (2007), 9, 1851-1854; Phys. Rev. B (2019), 100, 035439]. Therefore, we consider the present FFs to capture adsorption energetics at a level consistent with state-of-the-art DFT accuracy, and thus reliable for investigating interfacial dynamics. As the reviewer pointed out, further refinement of the FFs to a specific functional might improve the quantitative match. However, such re-parametrization would reduce the transferability of the FF. Moreover, in this work our focus is not on reproducing absolute maximal interfacial strengths during tensile deformation but on capturing the relative

conformational dynamics at PA/Al₂O₃ interfaces. For these reasons, we believe that the FF refinement is beyond the scope of this study and future work could explore functional-specific refinements. We have added the following sentences to the revised SI.

Added to Supplementary Note 6:

“The same optimization protocol as in the DFT calculations was used to estimate FF adsorption energies.”

“The deviations from GGA-PBE-D3 results are about 0.1–0.2 eV for PA6 and 0.2–0.3 eV for PAMXD6. Importantly, almost all FF adsorption energies fall within the error bars of the DFT calculations. Considering that, for organic molecules, typical errors in bond formation and adsorption energies on metal surfaces relative to experimental data are ~0.3 eV³ depending on the functional used, the FF results can therefore be regarded as being in good quantitative and qualitative agreement with the DFT results.”

3) New Section S9 (Supplementary Figures 10, 11): The statistics related to the values of local radius of gyration tensor components are rather poor. I recommend performing simulations of multiple independent configurations to strengthen the reliability of these findings.

Reply:

According to the reviewer’s suggestion, we performed additional statistical analyses of the local radius of gyration tensor components $R_{g,x}^L$, $R_{g,y}^L$, and $R_{g,z}^L$ for all four systems. Figure R3 shows the cumulative histograms of R_g^L ($s = 30$) for molecular chains located within 6.5 nm of the Al₂O₃ surface, obtained from five independent trajectories for each system. As $\varepsilon_z = 0.0$, the distributions of all three components are similar and centered near $R_g^L \approx 0.2 - 0.3$ nm. Upon increasing the strain to $\varepsilon_z = 0.2$, as indicated by red line, the distributions of $R_{g,z}^L$ broaden significantly, with higher probability densities within the range 0.6 – 1.1 nm, whereas the distributions of $R_{g,x}^L$ and $R_{g,y}^L$ remain almost unchanged in tail ends. This results in an increase of about 0.4–0.6 nm in the median R_g^L , quantitatively reflecting the local anisotropic extension of chain segments near the interface. These additional statistical results are fully consistent with the single-chain analysis shown in Supplementary Figs. 10 and 11, confirming that the strain-induced increase in the local radius of gyration $R_{g,z}^L$ occurs robustly across the four PA/Al₂O₃ systems. We have added these statistical results to Supplementary Fig. 12 of the revised SI.

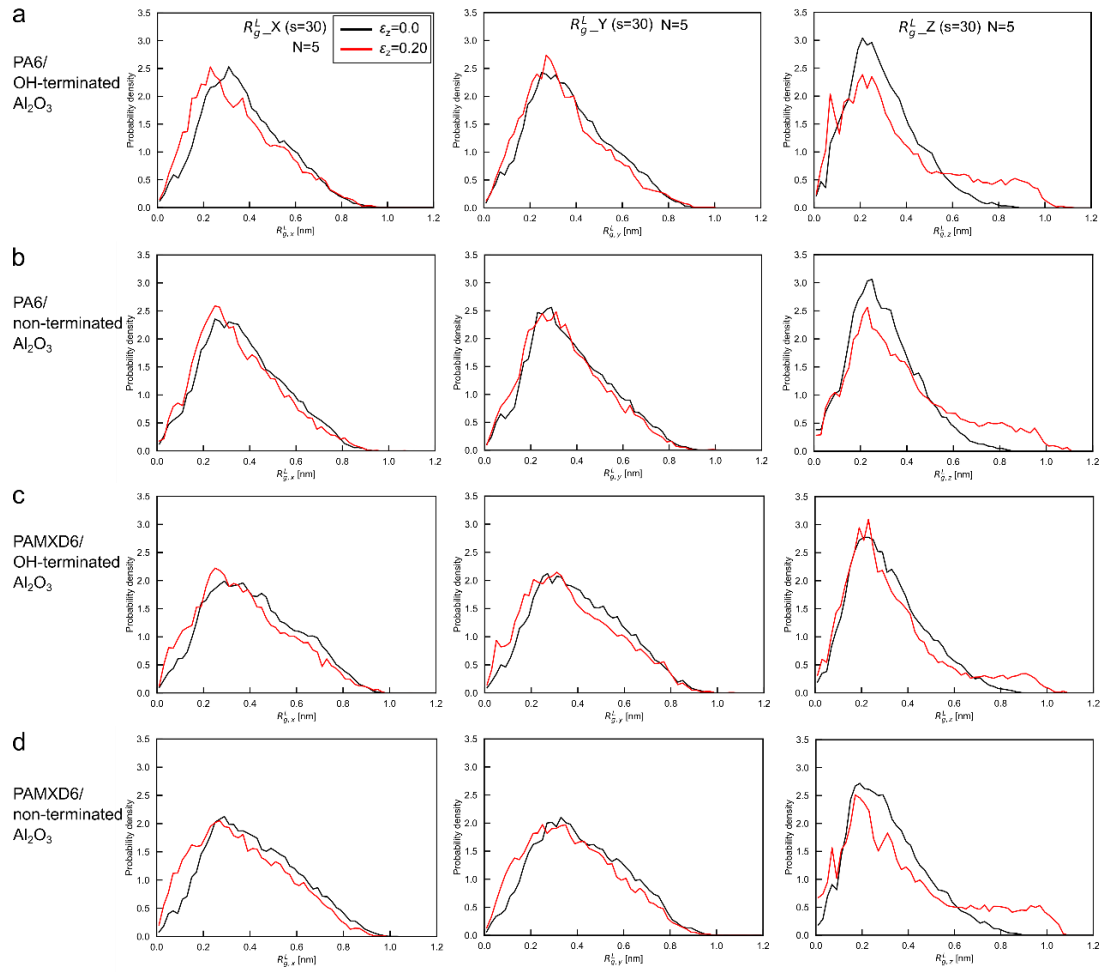


Figure R3. Probability distributions of the local radius of gyration R_g^L ($s = 30$) components for chains located within 6.5 nm of the substrate interface of four systems with five different initial configurations: a) PA6/OH-terminated model, b) PA6/non-terminated model, c) PAMXD6/OH-terminated model, d) PAMXD6/non-terminated model.

Added to page 13:

“The cumulative histograms of R_g^L ($s = 30$) obtained from five independent trajectories (Supplementary Fig. 12) confirm that this anisotropic local conformational change is statistically valid.”

Added to Supplementary Note 8:

“Supplementary Figure 12 shows the cumulative histograms of R_g^L ($s = 30$) for molecular chains located within 6.5 nm of the Al_2O_3 surface, obtained from five independent trajectories for the four PA/ Al_2O_3 systems. As $\varepsilon_z = 0.0$, the distributions of all three components are similar and centered near $R_g^L \approx 0.2 - 0.3$ nm. Upon increasing the strain to $\varepsilon_z = 0.2$, as indicated by red line, the distributions of $R_{g,z}^L$ broaden significantly, with higher probability densities within the range $0.6 - 1.1$ nm, whereas the distributions of $R_{g,x}^L$ and $R_{g,y}^L$ remain almost unchanged in tail ends. This results in an increase of about $0.4 - 0.6$ nm in the median R_g^L , quantitatively reflecting the local anisotropic extension of chain segments near the interface.

These additional statistical results indicate that the strain-induced increase in the local radius of gyration $R_{g,z}^L$ occurs robustly across all four systems.”

4) In the new section related to the glass transition temperature (S14. Effect of the difference between glass transition temperatures and MD simulation temperature) to demonstrate that the simulations were performed in the glassy regime, authors compute the mean squared displacements (MSDs) at 300 K and 1 atm over 10 ns (Supplementary Fig. 16c). MSDs naturally provide important information about the mobility of polymer chains, but it is not straightforward to relate this information with the actual T_g . more reliable approach would be to compute T_g from a “density vs. temperature” analysis via simulations across a range of temperatures. In addition, the presented MSD curves do not clearly exhibit the plateau-like behavior characteristic of glassy systems.

Reply:

We thank the reviewer for this helpful comment. Following the recommendation, we calculated the glass transition temperatures (T_g) of amorphous PA6 and PAMXD6 by analyzing the density–temperature relationships under NPT conditions (1 atm, controlled cooling/heating runs) for three independent samples. The low-temperature (glassy) and high-temperature (rubbery) regimes were fitted by linear regression, and the intersection was taken as T_g (Fig. R4). The results indicate that T_g is 327.7 ± 0.7 K for PA6 and 358.8 ± 0.8 K for PAMXD6, which are in close agreement with the experimental values obtained from DSC measurements (328.0 K for PA6 and 360.3 K for PAMXD6, see Supplementary Note 10). These findings confirm that our simulation protocol can reliably reproduce the absolute values as well as the relative trend of T_g between PA6 and PAMXD6, and ensure that the simulation temperature of 300 K used in the tensile tests lies well below T_g for both systems, validating that the models remained in the glassy state during mechanical deformation. Furthermore, regarding the MSD analysis (Supplementary Fig. 16c), we note that the curves of both PA6 and PAMXD6 show an initial rapid increase at short times, followed by leveling off into a near-plateau over the 16 ns observation window. Although a perfect plateau would require μ s-long relaxation times, which is accessible only with coarse-grained models, the absolute MSD values remain very small (0.02–0.08 nm²), indicating that atoms vibrate locally rather than diffusing over long distances. Taken together, these analyses demonstrate that both PA6 and PAMXD6 are in the glassy state under the present simulation conditions. We have added the results to the revised Supplementary Information. We have added these results to Supplementary Note 10 and Supplementary Fig. 20 of the revised SI.

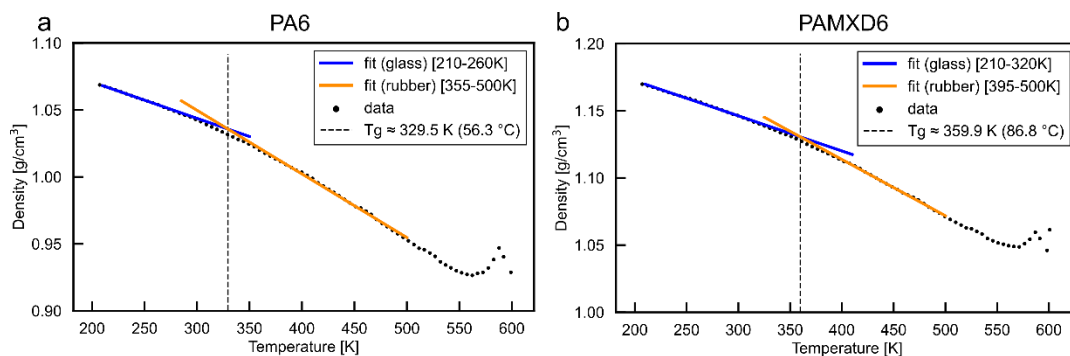


Figure R4. Temperature dependence of density for amorphous polyamide models. The glass transition temperatures T_g of a) PA6 and b) PAMXD6 were determined by fitting the low-temperature (glassy) and high-temperature (rubbery) regions with linear regressions and

defining the intersection as T_g . The T_g values are estimated as 358.8 ± 0.8 K for PA6 and 327.7 ± 0.7 K for PAMXD6. The simulations were carried out under NPT ensemble (1 atm, cooling/heating processes).

Added to Supplementary Note 10:

“We calculated the T_g of amorphous PA6 and PAMXD6 by analyzing the density–temperature relationships under NPT conditions (1 atm, controlled cooling/heating runs) for three independent samples. The low-temperature (glassy) and high-temperature (rubbery) regimes were fitted by linear regression, and the intersection was taken as T_g (Supplementary Fig. 20). The results indicate that T_g is 327.7 ± 0.7 K for PA6 and 358.8 ± 0.8 K for PAMXD6, which are in close agreement with the experimental values obtained from DSC measurements (328.0 K for PA6 and 360.3 K for PAMXD6). These analyses demonstrate that both PA6 and PAMXD6 are in the glassy state under the present simulation conditions.”

Reviewer #2:

Each comment has been responded to appropriately.

Reply:

Thank you for recommending our manuscript for publication.

Reviewer #3:

The authors have made adequate revision to address reviewers' comments.

Reply:

We appreciate your recommendation for publication of our manuscript.