

Beyond Lattice Matching: Steric Confinement Enables Enhanced Nucleation of Poly(L-lactide) on Nanotalc

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Electronic Supplementary Information

Abstract The incorporation of nucleating agents is widely regarded as an effective and practical strategy for overcoming the inherently slow crystallization rate of poly(L-lactide) (PLLA). While talc has long been used to promote PLLA crystallization, primarily attributed to lattice matching between its (002) crystal facet and PLLA crystals, the underlying nucleation mechanism remains inadequately understood. In this work, we employed exfoliated nanotalc with a high proportion of exposed (002) nucleation-active facets to enhance the crystallinity and accelerate the crystallization rate of PLLA and reveal new molecular-level insights into its nucleating mechanism. Compared to conventional talc, nanotalc significantly accelerated PLLA crystallization, increasing its crystallinity from 40.0% to 49.5% and reducing the half-crystallization time from 2.21 min to 1.18 min. Correlative *in situ* high-resolution transmission electron microscopy (TEM) and atomic force microscopy (AFM) established a definitive interfacial orientation relationship, showing that PLLA preferentially aligns along the talc [310] direction. Combined with *in situ* characterization and molecular dynamics simulations, these results demonstrate that the nucleation of PLLA is driven not only by lattice matching but also by steric confinement of PLLA methyl groups within the six-membered rings of SiO₄ tetrahedra on the talc facet, which strengthens interfacial interactions and facilitates nucleation. This study provides a molecular-level understanding of heterogeneous polymer nucleation and offers guiding principles for the rational design of high-efficiency nucleating agents.

Keywords Poly(L-lactide) (PLLA); Nanotalc; Nucleation-active facets; Crystal orientation; Steric confinement effect

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INTRODUCTION

Poly(L-lactide) (PLLA) is a promising biodegradable and biocompatible aliphatic polyester derived from renewable resources, such as corn and sugar beets.^[1–6] As a sustainable alternative to petroleum-based polymers, PLLA exhibits excellent thermomechanical properties and its market is steadily expanding.^[7–9] It is currently utilized in a wide range of applications, such as packaging materials,^[10–14] medical engineering materials,^[15–19] and agricultural films.^[20,21] Nevertheless, its broader application remains constrained by inherent shortcomings, namely, the relatively slow crystallization rate and low degree of crystallinity.^[22–25] To overcome these limitations, various strategies have been developed to promote PLLA crystallization, among

which the incorporation of nucleating agents has proven particularly effective.

To date, numerous nucleating agents have been investigated for PLLA crystallization and can be broadly classified into three categories: (i) organic compounds, such as TMC-series amides;^[26–29] (ii) macromolecular agents, including lignin,^[30] chitosan,^[31,32] starch,^[33,34] and cellulose crystals;^[35,36] (iii) inorganic agents, such as carbon nanotubes,^[37,38] zinc salts,^[22,23,25,39–41] montmorillonite,^[42,43] kaolin,^[44] and talc.^[3,45–48] Among the inorganic candidates, talc has emerged as one of the most widely used nucleating agents for PLLA, due to its low cost, commercial availability, and moderate nucleating efficiency.

Previous studies have attributed the nucleation ability of talc to epitaxial crystallization, primarily based on the lattice matching between the (002) crystal facet of talc and the α -form of PLLA crystals.^[3] This alignment is believed to reduce the interfacial free energy barrier for nucleation, thereby accelerating the crystallization. Despite its widespread use, talc

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still suffers from limitations, such as weak interfacial compatibility with PLLA and aggregation in polymer matrices, which often reduce its effective surface area and nucleation efficiency. Furthermore, the current understanding of the nucleation mechanism is largely phenomenological, and detailed molecular-level insights are lacking.

Herein, we report a new strategy for enhancing the nucleation efficiency of talc by preparing intercalation-exfoliated nanotalc with a high proportion of exposed (002) nucleation-active facets. Compared to conventional talc, nanotalc significantly improved PLLA crystallization behavior. More importantly, correlative *in situ* high-resolution transmission electron microscopy (TEM) and atomic force microscopy (AFM) were used to resolve the interfacial orientation relationship and confirm that PLLA aligned along the talc [310] direction. Molecular dynamics (MD) simulations were further employed to reveal a nucleation mechanism: the enhanced nucleation of PLLA is governed not solely by lattice matching but also by a steric confinement effect. Specifically, the methyl groups of the PLLA chains preferentially align with the six-membered rings of SiO_4 tetrahedra on the nanotalc surface, leading to interfacial interactions that promote crystal nucleation. This work not only offers a deeper understanding of the nucleation mechanism of PLLA on inorganic surfaces, but also provides valuable design principles for next-generation nucleating agents that integrate lattice matching with steric and conformational considerations at the molecular scale.

EXPERIMENTAL

Detailed experimental procedures, including materials, sample preparation, characterization methods, and molecular dynamics simulation details, are provided in the electronic supplementary information (ESI).

RESULTS AND DISCUSSION

Promoting Effect of Nanotalc on PLLA Crystallization

To enhance talc-induced nucleation in PLLA, exfoliated nanotalc with increased exposure of the (002) nucleation-active facets was prepared *via* an ultrasonication-assisted intercalation-exfoliation method. Transmission electron microscopy (TEM) and scanning electron microscope (SEM) images showed that the average size decreases from $(1.93 \pm 0.81) \mu\text{m}$ for conventional talc to $(543 \pm 204) \text{nm}$ for nanotalc (Figs. 1a, 1b and Fig. S2 in ESI), consistent with dynamic light scattering (DLS) result (588 nm). The atomic force microscopy (AFM) image indicated a thickness of 30–50 nm for the exfoliated nanotalc (Fig. 1c). X-ray diffraction (XRD) patterns (Fig. 1d) retained the characteristic (002), (004), and (006) reflections at 9.4° , 18.9° , and 28.6° , respectively, confirming that the talc crystal structure remained intact after ultrasonic exfoliation. Meanwhile, these diffraction peaks broadened, and the high-index diffraction peaks weakened or even disappeared, consistent with the reduced thickness and particle size.^[49,50] To quantitatively assess the change in accessible surface area following exfoliation, Brunauer-Emmett-Teller (BET) measurements were performed. The BET specific surface area of nanotalc was $24.91 \text{ m}^2/\text{g}$, approximately 4.5 times that of conventional talc ($5.55 \text{ m}^2/\text{g}$) (Fig. S2f in ESI). This increase is attributed to the increased accessibility of external basal surfaces,

which are predominantly composed of (002) facets owing to the platelet structure of talc. Together with the XRD and AFM results, the BET data therefore support that exfoliation increases the accessible area of the (002)-dominated basal surfaces, thereby providing more interfacial regions for heterogeneous nucleation.

Because the effective density of heterogeneous nucleation sites depends critically on the dispersion and interfacial contact of nucleating agents within the polymer matrix,^[51] the distribution of talc/nanotalc in the PLLA matrix was examined using SEM (Fig. S3 in ESI). Pure PLLA exhibited a smooth and featureless cryogenic fractured surface (Fig. S3a in ESI). When common low-polarity solvents (*e.g.*, dichloromethane) were used, conventional talc readily aggregated in the PLLA (Fig. S4 in ESI). To improve dispersion, acetone was used as a more polar solvent to prepare PLLA composites containing 1.0 wt% talc or 0.20 wt%–5.0 wt% nanotalc. Upon cooling after casting, PLLA rapidly gelled within approximately 1 min, immobilizing the fillers and suppressing sedimentation-driven aggregation during solvent evaporation. As a result, both talc and nanotalc exhibited improved distributions at low loadings (Figs. S3b–S3g in ESI). At nanotalc contents above 3.0 wt%, however, aggregation becomes evident (Figs. S3h and S3i in ESI), which is expected to reduce the accessible nucleating surface area. To establish a quantitative correlation between nanotalc aggregation and the accessibility of nanotalc surfaces, SEM images of cryo-fractured surfaces collected from multiple regions of composites containing 3.0 wt%, 4.0 wt%, and 5.0 wt% nanotalc were systematically analyzed. All discernible nanotalc particles were identified and classified (Figs. S5–S7 in ESI). The nanotalc4.0% composite contained several small aggregates (Fig. S6 in ESI), whereas increasing the loading to 5.0 wt% resulted in extensive aggregates, as highlighted by the black rectangular boxes (Fig. S7 in ESI). In addition, nanotalc5.0% exhibited several nanotalc-depleted regions, marked by red ellipses, indicating markedly poorer dispersion than that observed for nanotalc3.0% and nanotalc4.0%.

The number of nanotalc particles accessible to the PLLA matrix was estimated by excluding particles buried within aggregates from the total number of nanotalc particles identified in the SEM images (Table S1 in ESI). The estimated accessible nucleation numbers per field of view were 148.0 ± 6.1 (3.0 wt%), 196.0 ± 7.9 (4.0 wt%), and 188.0 ± 3.6 (5.0 wt%), following the order nanotalc4.0% > nanotalc5.0% > nanotalc3.0%. This trend indicates 4.0 wt% represents the optimum loading because it provides the optimal balance between increasing the total accessible nanotalc surface and maintaining adequate dispersion within the PLLA matrix. Although the total nanotalc content continues to increase at 5.0 wt%, extensive aggregation buries part of the nanotalc surface and generates nanotalc-depleted regions, thereby reducing the effective nucleating surface available for PLLA crystallization.

High-magnification SEM images also revealed interfacial voids at the talc/nanotalc–PLLA boundary (Figs. S3b and S3e in ESI), indicating limited interfacial compatibility. From a mechanical perspective, such interfacial voids may hinder efficient stress transfer across the PLLA–filler interface, act as local stress concentration sites, and facilitate interfacial

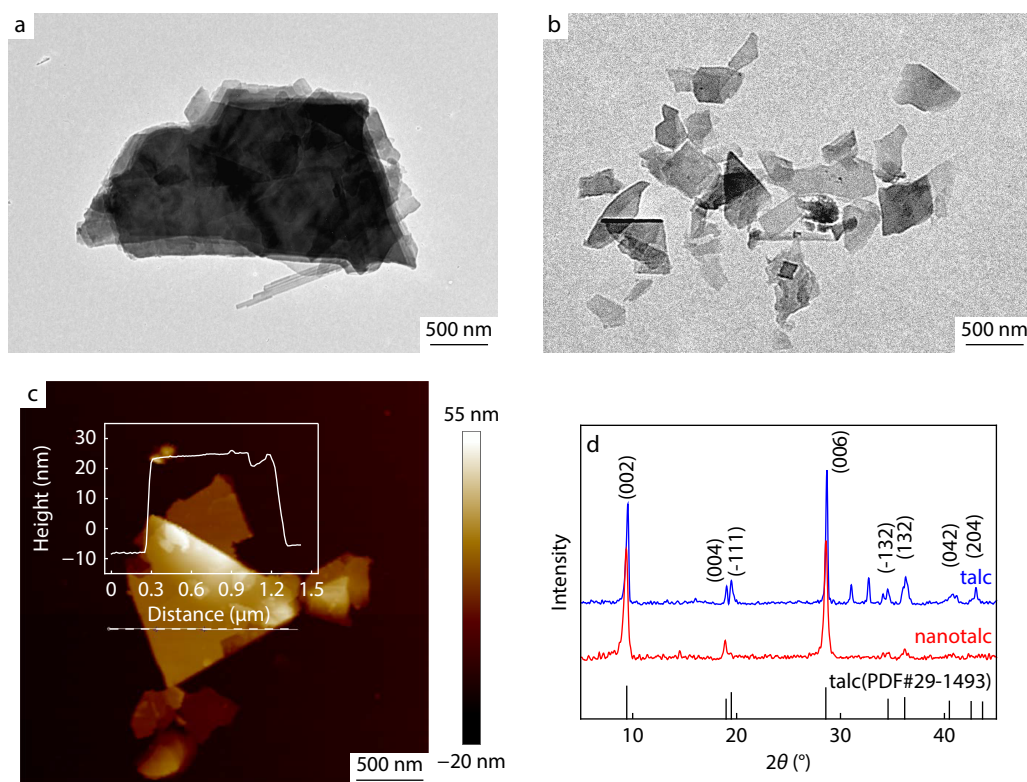


Fig. 1 Characterization of conventional talc and nanotalc. TEM images of (a) conventional talc and (b) nanotalc; (c) AFM image and height analysis of nanotalc; (d) XRD spectra of conventional talc and nanotalc.

debonding or crack initiation under mechanical loading. Therefore, although the mechanical properties were not the focus of this study, these interfacial defects could potentially compromise the strength, toughness, and long-term structural integrity of the composites.

The nucleation density and crystal morphology of PLLA induced by nucleating agents were visualized using polarized optical microscopy (POM) under isothermal conditions (130 °C) (Fig. 2). After 1 min, pure PLLA showed very few spherulites, which is consistent with its slow kinetics (Fig. 2a). In contrast, both talc and nanotalc substantially increased the number of nuclei and accelerated spherulite development (Figs. 2b–2h). The hot-pressing process during sample preparation partially aligns the two-dimensional nanotalc platelets within the PLLA matrix, which is consistent with the SEM observations. This alignment contributed to the preferred orientation of the PLLA crystals observed during the early stage of isothermal crystallization in the POM images. However, such a preferred orientation does not necessarily imply two-dimensional crystal growth because crystal growth can continue in multiple spatial directions after interfacial nucleation. Extending the isothermal crystallization time allowed clear observation of individual spherulites at relatively low nanotalc loadings (Fig. S8a in ESI). At higher nanotalc loadings, the increased nucleation density caused rapid impingement between neighboring spherulites, making their individual boundaries difficult to resolve (Fig. S8b in ESI). These observations indicate that the preferred crystal orientation and predominantly three-dimensional crystal growth can coexist, which is consistent with the Avrami exponent values ob-

tained from the isothermal crystallization analysis. The nucleation density increased progressively as nanotalc content increased from 0.2 wt% to 4.0 wt%, and then decreased at 5.0 wt% (Fig. 2i). The observable spherulite number density in the POM images followed the order nanotalc4.0% > nanotalc3.0% > nanotalc5.0%. This order differs from the number of accessible nanotalc particles derived from SEM analysis, which follows the order nanotalc4.0% > nanotalc5.0% > nanotalc3.0%. This difference is attributed to partial nanotalc aggregation and the formation of nanotalc-depleted regions in nanotalc5.0%, which led to a less homogeneous distribution of nucleation sites and fewer observable spherulites than in nanotalc3.0% after 1 min of isothermal crystallization, although the higher nanotalc loading still provided more accessible nanotalc surfaces overall than nanotalc3.0%.

To systematically investigate the effects of nanotalc on the crystallization behavior of PLLA, non-isothermal crystallization and melting behaviors were analyzed using differential scanning calorimetry (DSC, Fig. 3a and Fig. S9 in ESI). During cooling, pure PLLA exhibited only a weak crystallization exothermic peak at 96.1 °C, indicating its intrinsically sluggish crystallization (Fig. S9a in ESI). Incorporation of nanotalc produced a markedly stronger exotherm than conventional talc at the same loading (1.0 wt%), accompanied by a 4.8 °C increase in the melting crystallization temperature, T_{mc} and a 5.6% increase in melting crystallinity X_{mc} (Eq. S1 and Table S2 in ESI). As the nanotalc content increased, T_{mc} continued to rise, reaching a maximum improvement of 22 °C relative to pure PLLA. At higher loadings (≥ 5.0 wt%), T_{mc} began to de-

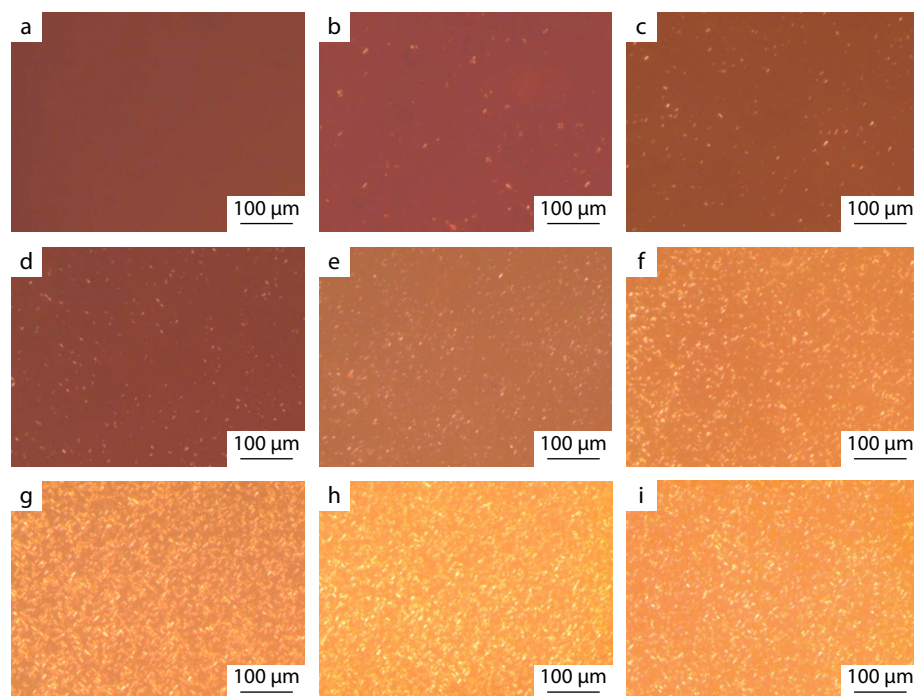


Fig. 2 POM photographs of pure PLLA and its composites with nucleation density isothermal crystallization at 130 °C for 1 min: (a) pure PLLA, (b) talc1.0%, (c) nanotalc0.2%, (d) nanotalc0.5%, (e) nanotalc1.0%, (f) nanotalc2.0%, (g) nanotalc3.0%, (h) nanotalc4.0%, and (i) nanotalc5.0%, respectively.

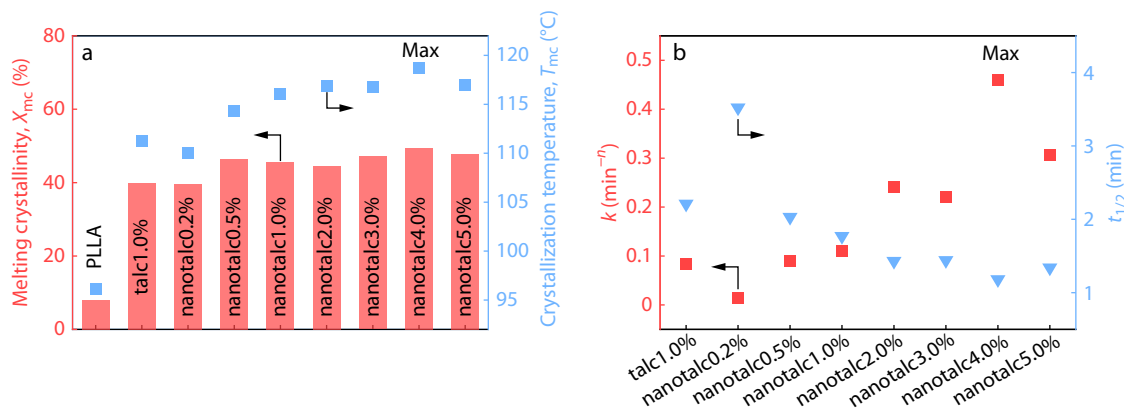


Fig. 3 (a) Melting crystallinity (X_m) and melting crystallization temperature (T_m) for pure PLLA and its composites; (b) The crystallization rate constant (k) and the half-crystallization time ($t_{1/2}$) of PLLA composites.

crease, consistent with the reduced nucleation efficiency expected from nanotalc aggregation observed by SEM and POM. Upon reheating (Fig. S9b in ESI), a pronounced cold crystallization peak appeared at approximately 106 °C, which was attributed to the recrystallization of PLLA. In contrast, no cold crystallization peaks were observed for the talc- or nanotalc-filled composites, suggesting enhanced crystallization during cooling. Compared with the POM results, DSC measures the bulk crystallinity developed throughout the non-isothermal cooling process. During this process, increasing the undercooling promotes additional nucleation, while continued crystal growth can partially compensate for the differences in the early stage spherulite density. Consequently, nanotalc5.0% retains a higher final crystallinity than nanotalc3.0%, although its crystallinity remains slightly lower than

that of the optimally dispersed nanotalc4.0%.

Isothermal DSC was performed at 130 °C (Fig. 3b and Fig. S10 in ESI). Pure PLLA exhibited a flat baseline with no discernible exothermic signal, even after 60 min of isothermal treatment (Fig. S11 in ESI), indicating extremely poor crystallization under these conditions. In contrast, nanotalc markedly accelerated isothermal crystallization and outperformed conventional talc (Fig. S10a in ESI). The relative crystallinity evolves into a characteristic sigmoidal pattern with time (Fig. S10b in ESI) and can be well described by the Avrami model (Eqs. S2–S4 in ESI), as evidenced by the linear Avrami plots (Fig. S10c in ESI). The fitted Avrami exponent n values ranging from 2.5 to 3.2.^[22] The Avrami exponent n reflects the combined effects of the nucleation mode and the effective crystal growth dimensionality. For two-dimensional growth,

the Avrami exponent n is typically approximately 2 for heterogeneous nucleation and 3 for homogeneous nucleation; for three-dimensional growth, n values of approximately 3 and 4 correspond to heterogeneous and homogeneous nucleation, respectively.^[52,53] At relatively low nanotalc loadings (≤ 3.0 wt%), the n values remain close to 3, indicating predominantly three-dimensional growth from heterogeneous nuclei. At 4.0 wt%, the substantially increased number of accessible nanotalc leads to a higher nucleation density and earlier interaction between neighboring growing crystals. This spatial constraint may contribute to the reduced apparent Avrami exponent ($n=2.5$), suggesting a deviation from ideal unrestricted three-dimensional growth. When the nanotalc loading was further increased to 5.0 wt%, n increased to 2.8. This partial recovery is attributed to the heterogeneous dispersion caused by severe nanotalc aggregation and the formation of nanotalc-depleted regions. Therefore, the variation in n reflects the combined effects of the nanotalc-induced nucleation density and spatial constraints imposed by the filler distribution. With increasing nanotalc content, the crystallization rate constant k increased and reached a maximum at 4.0 wt%, corresponding to the shortest half-crystallization time $t_{1/2}$ of 1.18 min (Eq. S5 and Table S3 in ESI). A common feature of all isothermal crystallization curves is an initial plateau, which corresponds to the nucleation induction time (t_i) of PLLA.^[23]

Nucleation Mechanism of PLLA on Nanotalc Surface

The above results demonstrate that nanotalc, with more nucleation-active (002) facets, markedly enhanced PLLA nucleation. However, the underlying mechanism remains to be clarified, particularly whether it is primarily based on lattice matching, specific interfacial interactions, or other local constraints at the polymer–talc interface. To address this question, the crystallization of PLLA on nanotalc was examined by correlative *in situ* TEM and atomic force microscopy (AFM),^[54–58] which provided direct access to the interfacial morphology and orientation.

The morphology of the PLLA crystals formed on the nanotalc surface was first characterized by AFM, as shown in Fig. 4. AFM height and phase images of PLLA cold-crystallized on nanotalc at 130 °C for 4 h reveal lamellae with six well-defined orientation directions separated by 30°, and can be grouped into two apparent six-fold orientation sets, marked

by blue and red guidelines in Figs. 4(b) and 4(c). The blue set is dominant, whereas the red set is less abundant, but remains clearly discernible. This orientational symmetry is consistent with the surface atomic structure of the nanotalc (002) crystal facets, where linked SiO₄ tetrahedra form a six-membered ring network.^[59] Accordingly, the observed lamellar orientations suggest epitaxy templating by specific crystallographic directions on the nanotalc (002) crystal facets.

To assign the lamellar orientations to substrate crystallography, *in situ* HR-TEM on nanotalc was used to correlate the lattice-resolved images with AFM maps (Fig. 5 and Fig. S12 in ESI). The thin single-crystal nature of nanotalc enables clear resolution of lattice fringes on the (002) facets, allowing identification of the [100] crystal direction (Fig. 5b). Correlative analysis with the AFM height map (Fig. 5c) shows that most PLLA lamellae align with the nanotalc [100] direction (blue dashed line), corresponding to the PLLA chain alignment along the nanotalc [010] direction (equivalent to the [310] direction). A minor population of lamellae followed an alternative orientation (red dashed lines). This orientation is consistent with that proposed by Stoclet *et al.*, despite the small lattice mismatch rate of 0.5% reported along one direction. However, the dominant orientation (blue dashed line) observed here is different,^[3] highlighting the need to consider additional interfacial factors beyond lattice-parameter matching.

Several nucleation mechanisms have been invoked to explain polymer nucleation, including chemical nucleation,^[60] physical nucleation,^[53,61,62] and conformational pre-ordering induced by additives.^[24,63,64] For talc-induced PLLA crystallization, hard epitaxy has often been invoked,^[3] in which a lattice mismatch below about 15% is considered favorable.^[65] However, lattice matching alone cannot capture the interfacial conformations and site-specific interactions that can bias chain alignment and nucleation. Our experimental observations indicate a highly selective interfacial orientation relationship, indicating the likely existence of additional interfacial constraints beyond lattice parameter matching. These considerations motivated a molecular-level analysis of how PLLA chains recognize nanotalc (002) crystal facets.

Two-stage computational simulations were conducted to elucidate the molecular origin of this orientation selectivity. First, a rigid-body molecular dynamics simulation of con-

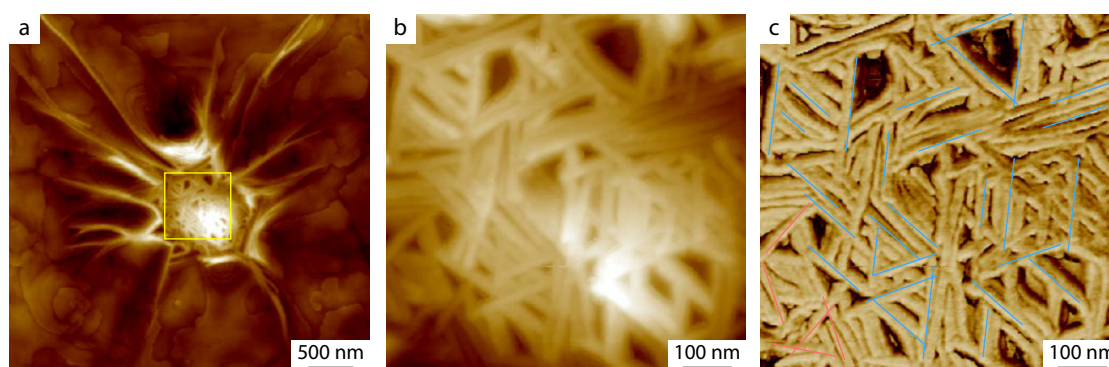


Fig. 4 Surface morphologies of PLLA cold-crystallized on nanotalc (002) crystal facets at 130 °C for 4 h revealed by AFM height (a, b) and phase (c) images. The yellow box in (a) marks the region shown at higher magnification in (b). Blue and red lines indicate two representative orientations of the PLLA lamella separated by 30°.

strained PLLA crystal chains on the (002) crystal facet of nanotalc was conducted, rendering the interactions at the polymer-substrate interface.^[66] Second, an all-atom molecular dynamics simulation was performed to investigate the dynamic processes of PLLA nucleation and crystallization. In molecular dynamics simulations, intramolecular interactions within PLLA, including bond stretching, angle bending, and dihedral torsion, were described using harmonic potentials. Non-bonded interactions are represented by the Lennard-Jones and electrostatic potentials. The force-field parameters and partial atomic charges for PLLA were taken from the model developed by McAliley and Bruce,^[67] while the atom types

and non-bonded parameters for the PLLA-nanotalc system were assigned following an OPLS-compatible force-field framework. The Lennard-Jones cross-interaction parameters between different atom types were obtained using the Lorentz-Berthelot combining rules.

In rigid-body MD simulations, crystalline PLLA chains with a left-handed 10_3 helical structure were allowed to translate and rotate on the nanotalc (002) facet, maintaining constant relative atomic positions and prohibiting bond rotations (Fig. S13 in ESI). The orientation angle was defined relative to the nanotalc [100] direction (0° in Fig. 6a). Statistical analysis over 20 ns revealed three dominant orientations at about 30° , 90° ,

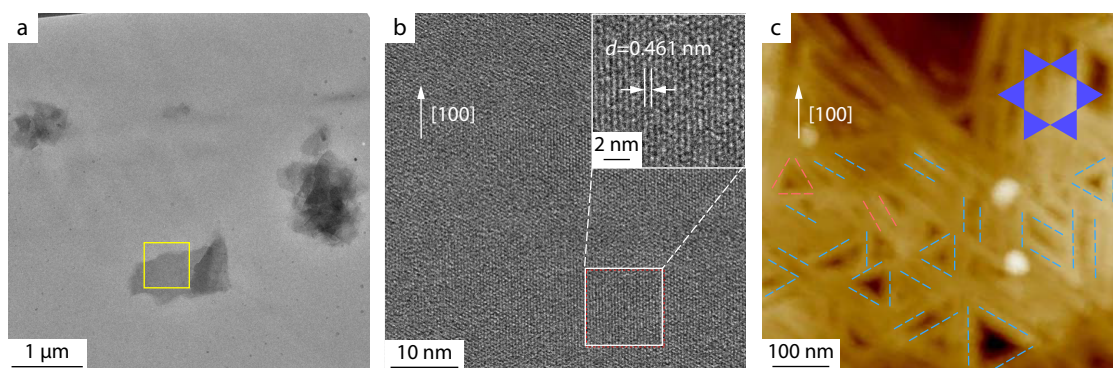


Fig. 5 (a, b) HR-TEM images of nanotalc. The yellow box in (a) marks the region correlated with the AFM map in (c). (c) AFM height image of PLLA cold-crystallized on nanotalc (002) crystal facets at 130°C for 4 h. The arrows indicate the nanotalc [100] crystal direction on the (002) crystal facets of nanotalc.

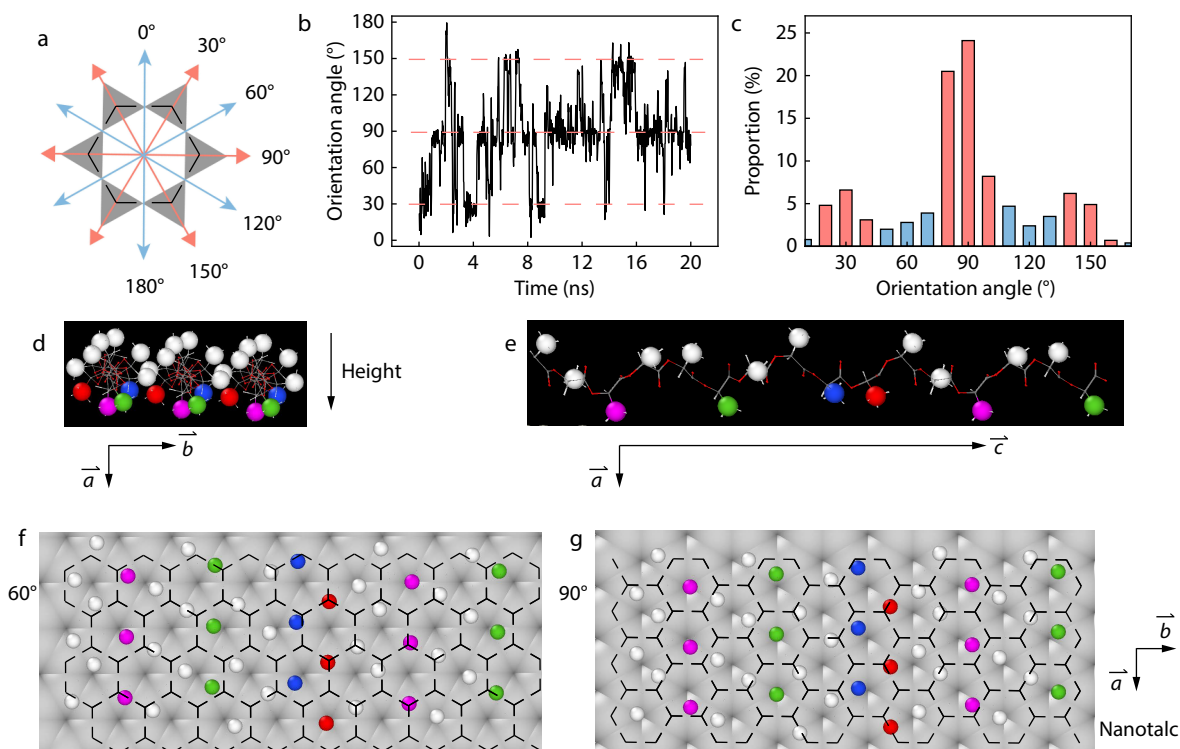


Fig. 6 (a) Definition of model angles; (b, c) Line graph and columnar statistical chart of running results of rigid-body molecular dynamics simulation; (d, e) Front and side views of three PLLA crystal chains (sourced from the CIF file of PLLA crystals); (f, g) The real position of methyl groups of the PLLA crystal chains on the surface of nanotalc (rigid-body molecular dynamics simulation). Only the methyl groups in the crystalline PLLA chain are displayed, and the methyl groups are represented by spheres. The different colors of the spheres represent the different heights of the methyl groups. The hexagon represents the hexagonal structure composed of SiO_4 tetrahedra.

and 150°, which corresponded to the [310] direction of the nanotalc, whereas 0°, 60°, and 120° were disfavored (Figs. 6b and 6c in ESI). This distribution matches the interfacial orientations observed experimentally, indicating that the nanotalc surface imposes a strong orientational selection. Considering the left-handed 10₃ helical structure of crystalline PLLA and the spatial distribution of its pendant methyl groups (Figs. 6d and 6e), we propose that the methyl groups on the bottom face of the helix preferentially anchor to the nanotalc surface. Specifically, these methyl groups tend to be sterically located on the six-membered rings formed by SiO₄ tetrahedra on the (002) crystal facet of the nanotalc. Orientations of 30°, 90°, and 150° maximize this ring occupancy relative to 0°, 60°, and 120°, respectively (Figs. 6f, 6g and Fig. S14 in ESI). Importantly, the same preferred orientations also enabled favorable lattice matching. When the PLLA chains align along the nanotalc [310] direction, the *c*-axis length of the PLLA lattice (2.886 nm) is approximately three times the *b*-axis length of the nanotalc lattice (0.910 nm), resulting in a lattice mismatch of only −5.4%. A near-commensurate relation was also obtained when four unit cells along the *b*-axis length of the PLLA lattice (0.617 nm) matched five repeats along the *a*-axis of the nanotalc lattice (0.526 nm), with a mismatch of −6.2%. Thus, lattice matching was realized on the sterically preferred orientations, supporting a cooperative picture of steric confinement and an epitaxy-like registry.

Density functional theory (DFT) calculations further quantified the orientation-dependent stability. For rigid PLLA chains on the nanotalc (002) crystal facet, the adsorption energies at

30°, 90°, and 150° were −3.93, −3.98, and −3.49 eV, respectively, which were more negative than those at 0°, 60°, and 120° (−3.10, −3.15, and −3.18 eV, respectively) (Fig. S14 and Table S4 in ESI), indicating stronger binding at the sterically favored orientations. These results indicate that the experimentally observed orientations correspond to more favorable polymer–surface interactions, where the methyl groups of PLLA can better accommodate the six-membered rings formed by silicon-oxygen tetrahedra on the nanotalc surface. This stabilization arises from a higher population of methyl groups facing and packing into the surface rings at 30°, 90°, and 150°, which is consistent with the steric confinement picture inferred from rigid-body MD simulations.

All-atom MD simulations performed without structural constraints were conducted to test whether the preferred interfacial orientations persisted dynamically. Two initial configurations were compared: one started at 30° (favored by rigid-body MD simulations) and the other at 0° (Fig. S15 in ESI).^[3] Although direct crystal nucleation is beyond the accessible simulation time, polymer segments adsorbed on nanotalc exhibit clear orientational bias: about 70% of PLLA chains in the 30° model adopt 30°, 90°, or 150°, whereas only about 50% do so in the 0° model (Fig. 7a, Figs. S16 and S17 in ESI). Analysis of the methyl group positions showed that interfacial methyl groups were concentrated at lower heights near the surface ring sites (Fig. 7b, Figs. S18 and S19 in ESI). Specifically, the interacting methyl groups were located at (0.388±0.005) nm (30°) and (0.394±0.008) nm (0°), which were lower than the non-interacting methyl groups at (0.451±0.008) nm (30°) and

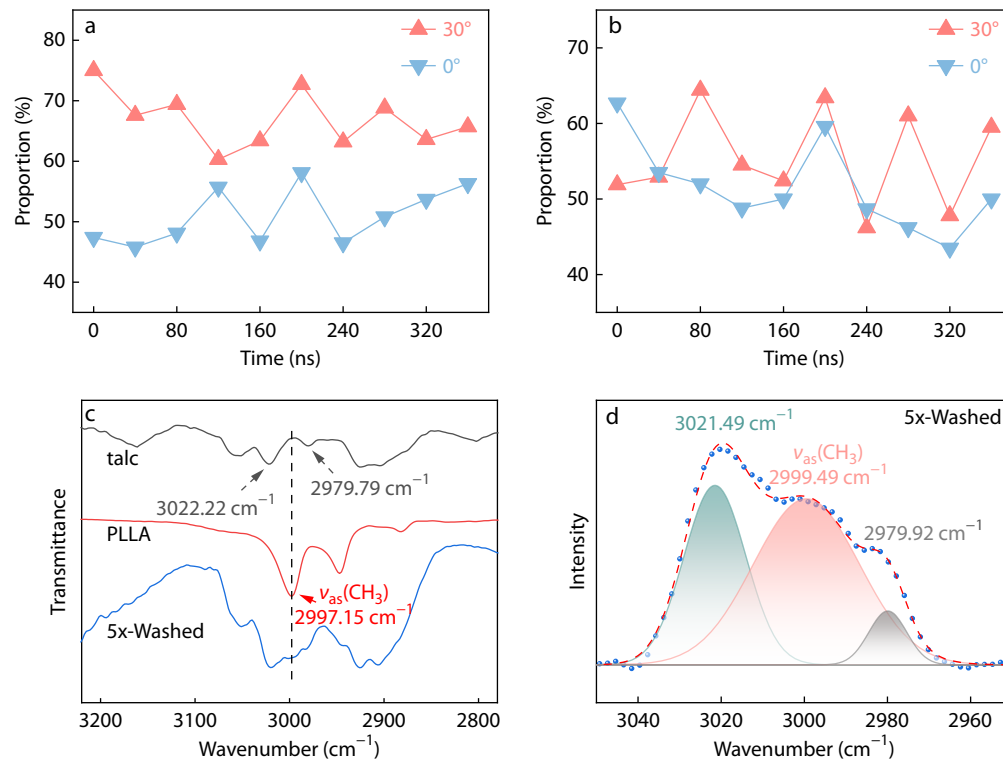


Fig. 7 (a) Trend chart of orientational proportion of PLLA chains over time; (b) Trend chart of the proportion of methyl groups in the hexagonal ring formed by silicon-oxygen tetrahedra over time; (c) FTIR spectra of talc, PLLA, and the PLLA/talc composite after 5 washing cycles; (d) Peak deconvolution of the 5x-washed sample shown in Fig. 7(c). The blue dots represent the experimental spectrum, the red dashed line represents the overall fitted spectrum, and the colored lines denote the individual fitted components.

(0.454 ± 0.006) nm (0°), indicating stronger interfacial engagement (Fig. S20 in ESI). To experimentally validate the methyl-group confinement suggested by the simulation, an *in situ* Fourier transform infrared (FTIR) analysis was performed (Fig. 7c and Fig. S21 in ESI). Pure PLLA exhibits the $-\text{CH}_3$ asymmetric stretching vibration (ν_{as}) at 2997.15 cm^{-1} , whereas PLLA/talc composites show a blue shift (2.34 cm^{-1}) of this peak (Fig. 7d), consistent with reduced motional freedom and increased local rigidity of methyl groups at the interface. Together with the simulation results, these data support the steric confinement of PLLA methyl groups within the nanotalc surface rings as key contributors to interfacial recognition and nucleation.

Based on these results, three points deserve further investigation. First, the enhanced nucleating ability of nanotalc does not simply arise from the reduction of talc to the nanoscale. Rather, it is closely associated with increased exposure of nucleation-active (002) facets, highlighting nucleation-active facet exposure as an important factor in the design of new nucleating agents. Second, the correlative *in situ* TEM/AFM results showed that PLLA adopts a preferred interfacial orientation that cannot be fully rationalized by conventional lattice parameter matching alone. Even when a minimal lattice mismatch is obtained by calculation from the unit-cell comparison, the corresponding orientation does not necessarily dominate the nucleation process, indicating that additional interfacial structural information must be considered. Third, although previous studies have suggested that steric effects from methyl groups in polymer chains may influence nucleation and crystallization, our molecular dynamics simulations, based on the experimentally determined interfacial orientation, provide further molecular-level insights into the methyl-group confinement effect. Although complete atomic-scale resolution of the interface between a complex helical polymer and an inorganic nucleating surface remains challenging, the combined experimental and simulation results support local steric confinement between the PLLA methyl groups and the six-membered rings on the talc (002) facets as a reasonable molecular-level contribution to the observed orientation selection and nucleation enhancement.

CONCLUSIONS

In summary, this work demonstrates that nanotalc effectively promotes PLLA crystallization by increasing the exposure of nucleation-active (002) facets. Compared with conventional talc, nanotalc accelerates crystallization, increases crystallinity, and improves the nucleation density. Correlative *in situ* TEM and AFM further revealed the preferred interfacial orientation of PLLA on the nanotalc surface, indicating that the interfacial structure plays an important role in the nucleation process. Molecular simulations and FTIR analysis provided supportive evidence for local polymer-surface interactions at the nanotalc interface, including possible steric effects associated with PLLA methyl groups. These results deepen our understanding of PLLA nucleation on mineral surfaces and provide useful guidance for the design of efficient nucleating agents for semicrystalline polymers.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-026-3840-1>.

Data Availability Statement

Data supporting the findings of this study are available from the corresponding author upon reasonable request.

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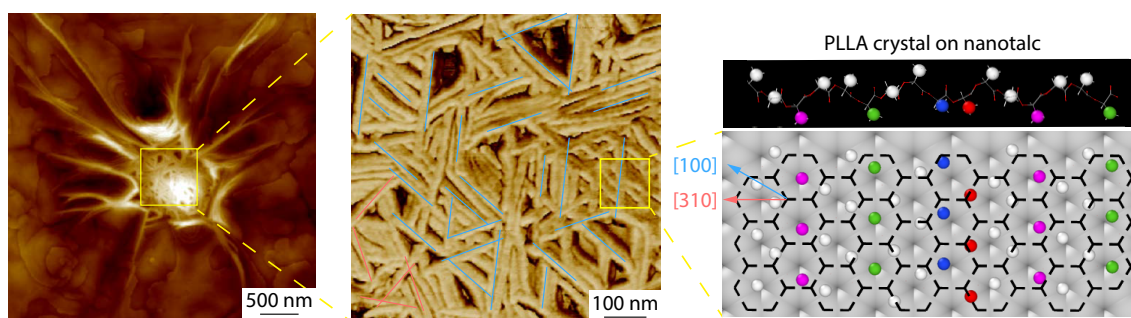
Graphical Abstract

Beyond Lattice Matching: Steric Confinement Enables Enhanced Nucleation of Poly(L-lactide) on Nanotalc

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Exfoliated nanotalc exposes more nucleation-active (002) facets and promotes poly(L-lactide) (PLLA) nucleation, with PLLA preferentially oriented along the nanotalc [310] direction. Beyond lattice matching, steric confinement of PLLA methyl groups within the six-membered rings of SiO_4 tetrahedra on the nanotalc (002) facets strengthens the polymer-surface interactions, accelerating crystallization and increasing crystallinity.



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