

Simulation of the Specific Contributions of Molecular Weight, Orientation Degree, and Crystallinity to the Tensile Mechanics of Polyethylene Fibers

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Electronic Supplementary Information

Abstract UHMWPE fibers exhibit impressive modulus and strength, but they have not reached their theoretical limits. Researchers focus on molecular weight, orientation, and crystallinity of UHMWPE, yet their contributions to mechanical properties are unclear. Molecular dynamics simulations are valuable but often limited by computational constraints. Our aim is to simulate higher molecular weights to better represent real UHMWPE fibers. We used Packmol and Polyply methodologies to construct PE systems, with Polyply reproducing more reasonable properties of UHMWPE fibers. Additionally, tensile simulations showed that orientation and crystallinity greatly impact Young's modulus more than molecular weight. Energy decomposition indicated that higher molecular weights lead to covalent bonds that can withstand more energy during stretching, thus increasing breaking strength. Combining simulations with machine learning, we found that orientation has the most significant impact on Young's modulus, contributing 60%, and molecular weight plays the most crucial role in determining the breaking strength, accounting for 65%. This study provides a theoretical basis and guidelines for enhancing UHMWPE's modulus and strength.

Keywords Molecular dynamics simulation; Polyethylene fiber; Mechanical properties

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INTRODUCTION

Polyethylene (PE), the simplest semi-crystalline polymer material, boasts excellent properties and wide-ranging application prospects.^[1–3] Current research in polyethylene (PE) is concentrated on developing high-strength and high-modulus PE products. Ultra-high molecular weight polyethylene (UHMWPE) fibers, due to their exceptionally high molecular weight and unique internal structure, fulfill these criteria and have attracted considerable attention.^[4–6] However, the highest tensile strength and modulus of UHMWPE fibers experimentally achievable still fall short of their theoretical maximum values.^[7,8] To increase the mechanical properties of UHMWPE fiber, extensive research has focused on three critical factors influencing the modulus and strength of UHMWPE fibers: molecular weight, orientation, and crystallinity.^[9–15] While due to the mutual influence between these factors, it is not yet known which key factor has the greatest impact on breaking strength and Young's modulus. Consequently, understanding the interplay between

molecular weight, degree of orientation, and crystallinity is essential for optimizing PE fibers' performance.

Molecular dynamics (MD) simulations are crucial for exploring the complex connection between polymer structure and properties, offering detailed insights into polymer behavior under different circumstances.^[16–23] By constructing a fully crystalline PE model with short chains in periodic boundary conditions, researchers can approximate the modeling of UHMWPE fibers in simulation.^[24–28] However, UHMWPE fibers are essentially semi-crystalline polymers in experiments. The ideal crystalline PE model cannot fully capture the impact of long molecular chains on the structure and mechanical properties of PE fibers. Therefore, simulation studies on semi-crystalline PE are necessary. The time scales of MD simulations are generally too short to observe the crystallization nucleation in PE melts.^[29–32] However, by stretching and orienting the PE melt, we can accelerate the crystallization process of PE, allowing for observation on the MD simulation time scale.^[33–37] Lavine *et al.*^[29] conducted uniaxial stretching and isothermal crystallization experiments on PE, demonstrating the effectiveness of uniaxial stretching in promoting the nucleation of PE crystallization. Slitzberg *et al.*^[38] studied the effect of strain rate on the orientation, stretchability and crystallinity of entangled PE during uniaxial stretching, and were

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able to prepare semi-crystalline PE with a crystallinity of nearly 50%. Yamamoto *et al.*^[39,40] prepared PE fibers through stretching and isothermal crystallization of PE melts. He examined the development of the crystal structure within the fibers, as well as the mechanical deformation process along the fiber axis. Hagita *et al.*^[41] achieved varying pre-elongation in PE through stretch-induced crystallization in larger-scale PE systems. The elastic modulus of the PE model increases with increasing pre-elongation, which indicates that the pre-elongation determines the crystal structure and mechanical properties.

Due to the limited computing power of computers, most research on semi-crystalline PE models focuses on molecular weights under 1×10^4 g/mol.^[42,43] Simulating UHMWPE presents challenges, but we aim to push the boundaries by using coarse-grained models that include molecular details. To achieve this, we utilize the Martini force field, and the semi-crystalline PE is constructed using two different methodologies: Packmol and Polyply. Packmol^[44,45] is an open-source software tool designed for efficiently packing an entire equilibrated polymer chain into a simulation box without causing overlaps between the molecules. Polyply^[46] is a python suite that can generate coordinates of polymer systems directly by random walk algorithm. Different modeling approaches can produce different initial structures in simulations, potentially affecting the final structural characteristics, especially in UHMWPE models.

We evaluated and compared the thermodynamic and mechanical properties of PE models produced by these two methods, and found that Polyply-built PE serves as a good representative of UHMWPE. This model was subsequently stretched to form fibers, which were used to investigate how molecular weight, orientation, and crystallinity affect the breaking strength and Young's modulus of UHMWPE fibers. The energy of the fibers during tensile testing was analyzed to highlight the role of high molecular weight in improving fiber breaking strength. Machine learning techniques were employed to quantify the impact of these factors on the fibers' strength and modulus, and to calculate the percentage contribution of each factor to Young's modulus and breaking strength.

SIMULATION METHODOLOGY

The molecular configuration of PE is modeled using the Martini coarse-grained (CG) model,^[47] where each CG bead corresponds to four methylene groups. In Martini simulations, the

cutoff value for LJ interactions is 1.1 nm. A time step of 20 fs was applied. Apply the v-rescale algorithm for temperature control and couple pressure using a Berendsen barostat. All simulations were carried out utilized Gromacs version 2021.4.^[48] VMD 1.8.2 (Visual Molecular Dynamics) for the visualization.^[49] For the comparison of mechanical properties of semi-crystalline PE structures of different lengths, each box contains 300000 Martini beads with varying chain lengths and numbers. Packmol and Polyply were used to build the initial simulation structures, with the box sizes of $32 \text{ nm} \times 32 \text{ nm} \times 32 \text{ nm}$. Details of PE systems are listed in the Table 1.

The Packmol model is constructed by first generating a coordinate file of a single molecular chain from python code, followed by 5000 steps of energy minimization and equilibration. A specific number of PE molecular chains are duplicated and packed into a box with a side length of 1000 nm using the Packmol program and then energy minimization is performed. Subsequently, the box undergoes compression at 1000 bar for a duration of 10 ns at a temperature of 500 K, followed by further compression at 100 bar and then at 50 bar, each for 10ns. Once the size of the box is reduced to approximately $100 \text{ nm} \times 100 \text{ nm} \times 100 \text{ nm}$, the system is equilibrated for 1 μs at 1 bar. Then the compression process continued until the box size was reduced to $32 \text{ nm} \times 32 \text{ nm} \times 32 \text{ nm}$. The Polyply suite generates the coordinates of the PE models directly.

For all PE systems, energy minimization is conducted for 5000 steps using the steepest descent algorithm. The systems are then equilibrated at $T=500 \text{ K}$ for 10 μs , followed by cooling at a rate of 2.5 K/ns to 300 K. Subsequently, the systems are further equilibrated at 300 K for 10 μs . The well-balanced systems undergo hot stretching at 400 K with a stretching rate of 0.001 nm/ps. The stretched melts are cooled at a rate of 1 K/ns to 300 K, followed by equilibration for an additional 10 μs , resulting in the formation of PE fibers with varying pre-elongation. The pre-elongation of fibers is defined as:

$$\lambda = \frac{L_k - L_0}{L_0} \quad (1)$$

where the L_0 is the original length of the model along the hot-stretching direction, and L_k is the length of the fiber after hot-stretching.

The glass transition temperature (T_g) is determined by analyzing the volume's temperature-dependent changes. The well-balanced systems are heated to 450 K to equilibrium for 5 μs and cooled from 450 °C to 50 °C at a rate of 0.1 K/ps. T_g is estimated by linearly fitting the endpoints of the curve and identifying the intersection point of these two linear trends.

Table 1 Simulation details of PE systems.

Packmol	Chain length	Number of chains	Molecular weight (g/mol)	Polyply	Chain length	Number of chains	Molecular weight (g/mol)
1	100	30000	5.6×10^3	1	250	1200	1.4×10^4
2	250	1200	1.4×10^4	2	600	500	3.36×10^4
3	600	500	3.36×10^4	3	1000	300	5.6×10^4
4	750	400	4.2×10^4	4	5000	60	2.8×10^5
5	1000	300	5.6×10^4	5	10000	30	5.6×10^5
6	5000	60	2.8×10^5	6	20000	15	1.12×10^6
7	6000	50	3.36×10^5	7	30000	10	1.68×10^6
8	10000	30	5.6×10^5	8	60000	5	3.36×10^6

The mechanical properties of the PE fibers are analyzed by stretching them at room temperature with a stretching rate of 0.005 nm/ps. The stress-strain curves of PE with different molecular weights are obtained to analyze the mechanical properties. The Young's modulus is determined by analyzing the slope of the stress versus strain curve within the linear regime (less than 3% strain). The tensile strength, on the other hand, refers to the stress level at which the material undergoes fracture.

The end-to-end distance is calculated as the average distance between the ends of each molecular chain in the system. The radius of gyration is a metric used to determine the average radius of the system's mass distribution, defined as:

$$R_g = \sqrt{\frac{\sum_i m_i (r_i - r_c)^2}{\sum_j m_j}} \quad (2)$$

where m_i is the mass of the i^{th} bead, r_i is the coordinate of the i^{th} bead, r_c is the centroid of the molecular chain.

The chord vector for bead i is given by the vector extending from bead $(i - 1)$ to bead $(i + 1)$. And the degree of orientation^[29,39,40,50,51] along the fiber axis z is defined as:

$$P_{2z} = \left\langle \frac{3\cos^2\theta_{iz} - 1}{2} \right\rangle \quad (3)$$

where θ_{iz} is the angle between the chord vector of bead i and the z -axis.

The local order parameter P_2 and crystallinity of fiber^[31,52,53] is defined as:

$$P_2 = \left\langle \frac{3\cos^2\theta_{ij} - 1}{2} \right\rangle \quad (4)$$

where the ensemble average was taken over all beads j , within the cutoff distance r_c from bead i , where θ_{ij} is the angle formed by the chord vector of bead i and the chord vector of bead j , respectively. We determine the crystallinity (X_c) by identifying the largest cluster that exceeds the threshold ($P_2 > 0.4$) and is spatially adjacent within the system. The ratio of beads in the largest bead cluster to the total bead count is referred to as crystallinity.^[40,54,55]

In this study, we utilized the Z1+ code for conducting a primitive path analysis to assess the level of entanglement.^[56] The Z1+ code scrutinizes the primitive path network of a snapshot and identifies Z values, which represent the number of kinks present in each polymer chain. The entanglement degree of PE models can be characterized based on these Z values.

Following the simulations, the Scikit-learn machine learning (ML) package^[57] was employed to examine the mechanical characteristics of PE derived from the simulations. Machine learning was applied to assess how factors like molecular weight, orientation, and crystallinity affect the strength and modulus of PE fibers. Different regularization techniques, including Linear regression, LASSO regression,^[58] ridge regression,^[59] and elastic-net,^[60] were assessed for the linear regression models. Moreover, non-linear regression models such as voting regressor,^[61] stacking regressor,^[62] polynomial regression, XGBoost regression, tree regression, random forest regression and neural network regression were also used. The base learners of the voting regression model include

LASSO regression, ridge regression and elastic net regression. And the base learners of the voting regression model include LASSO regression, ridge regression, elastic-net regression and the meta-model was voting regressor. The dataset is divided into two sets, with 2/3 of the data used as the training set and 1/3 used as the test set. We calculate the coefficient of determination R^2 and root mean square deviation RMSE for each model to evaluate its rationality. The equation fitted by the best regression model is selected to quantify the percentage contribution of each factor to Young's modulus or breaking strength. The coefficient corresponding to each factor divided by the sum of the coefficients of the three factors is the percentage contribution of this factor.

The determination coefficient and root mean square error are employed to assess the fitting performance of the model. The determination coefficient is defined as:

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad (5)$$

where $\hat{y}_i$ is the predicted value and $\bar{y}$ is the average value, n represents the number of samples. The root mean square error (RMSE) is defined as:

$$\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2} \quad (6)$$

RESULTS AND DISCUSSION

Model Validation

To evaluate whether the high molecular weight PE systems can qualitatively represent UHMWPE, we assessed their thermodynamic and mechanical properties and compared these measurements with values from other simulations and experimental studies. Two different methods were employed to construct the PE systems: utilizing either the Packmol or the Polyly package. The systems were equilibrated for 10 μs followed by annealing at 500 K for 10 μs (details in method section). The transition temperature T_g is determined by cooling the systems to 50 K (see Figs. S1 and S2 in the electronic supplementary information, ESI, and Fig. 1a), while the density is calculated at 300 K (see Fig. 1b). The T_g of both PE models range from 270 K to 285 K (Figs. S1 and S2 in ESI and Fig. 1a), consistent with other simulation studies which typically report values in the range of 250–300 K.^[19,31,63,64] Additionally, as the molecular weight of the polymers increases, T_g value also increases. This trend aligns with experimental findings.^[65,66] The density of both PE simulations at 300 K is approximately 866 kg/m³, also closely matching values reported in other studies.^[47,67]

The T_g and density exhibited by the coarse grain models^[19,47,63,67] differ from those observed for UHMWPE in experimental studies.^[65,68–71] The discrepancy in T_g may arise from the influence of cooling rates on the glass transition temperature; specifically, the higher cooling rates employed in simulations often result in T_g values that are elevated compared to those obtained experimentally. Moreover, coarse-grained models reduce system complexity by combining multiple atoms into a single coarse-grained particle. This approach decreases the level of interdigitation between atoms and may lead to inaccuracies in the simulation's density.

After applying stress to the equilibrated systems, the stress-

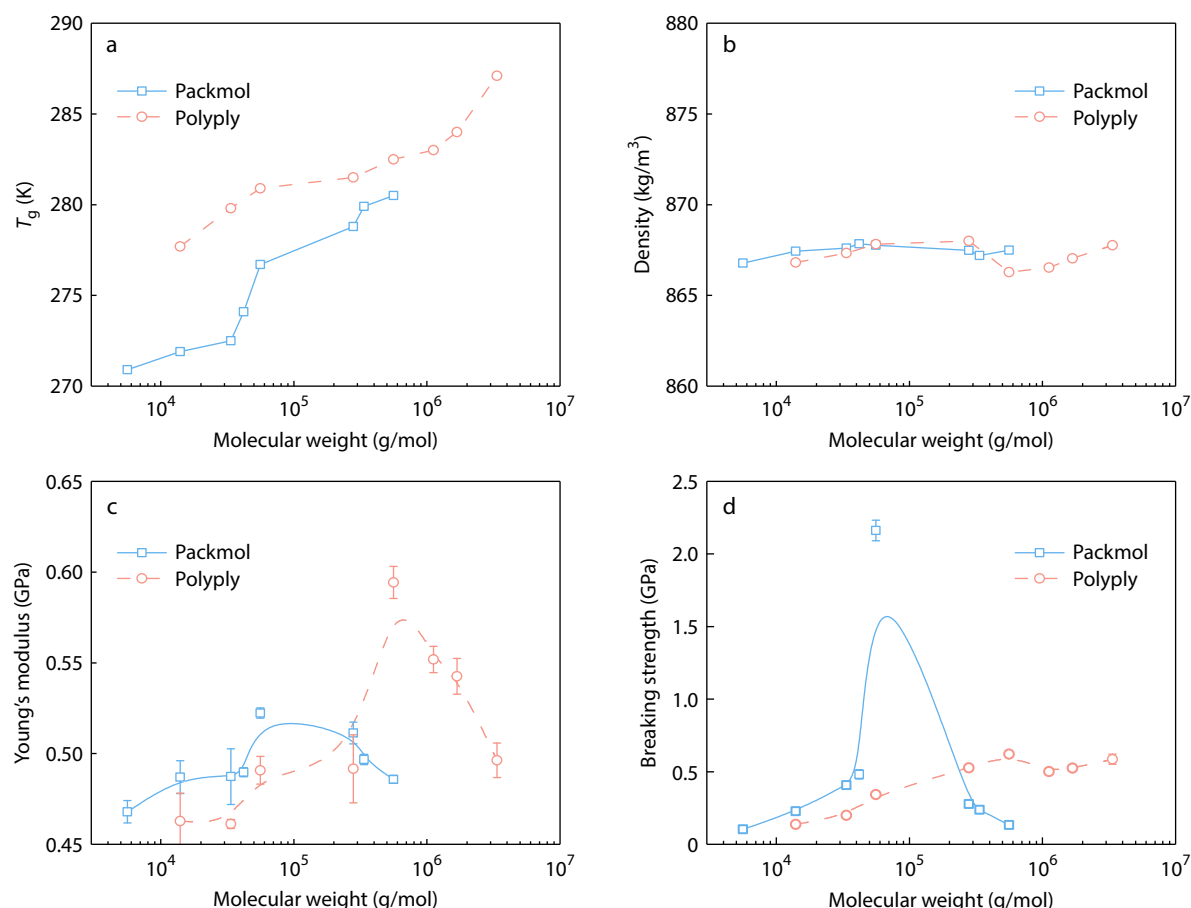


Fig. 1 (a) T_g and (b) density of PE models built with two approaches, Packmol and Polyply, as a function of molecular weight. Mechanical properties of PE systems constructed with Packmol and Polyply: (c) Young's modulus versus molecular weight and (d) breaking strength versus molecular weight.

strain curve, Young's modulus, and breaking strength of the balanced PE model at 300 K are calculated and presented in Fig. S3 (in ESI) and Figs. 1(c) and 1(d). For both PE systems, the Young's modulus and breaking strength, in general, increase with molecular weight. This trend agrees with experimental results,^[72–74] and the absolute values of Young's modulus and breaking strength are on the same order of magnitude as other simulation reports.^[19,21,22,39,75]

However, in systems built with the Packmol package, once the molecular weight reaches 5.6×10^4 g/mol, the Young's modulus and breaking strength begin to decrease (Fig. S3 in ESI and Fig. 1). A similar decrease also occurs in systems built with Polyply, but it happens at higher molecular weights (5.6×10^5 g/mol). For molecular weights below these two values, PE exhibits similar thermodynamic and mechanical properties to those of UHMWPE in experiments.^[76–78] Therefore, our simulation provides a reasonable representation of UHMWPE.

The systems built with Packmol and Polyply exhibit unreasonable mechanical properties beyond a certain molecular weight, which limits our research on PE systems with higher molecular weight. To address the concerns in high molecular weight systems, we examined the factors related to the mechanical properties of PE across different molecular weights. The degree of orientation (Fig. 2a), crystallinity (Fig. 2b) and

the number of entanglements per chain (Fig. 2c) are calculated. The changes in degree of orientation and crystallinity values of the two PE systems with increasing molecular weight are minimal, with absolute values close to zero. However, for the systems built with Packmol, as the molecular weight exceeds 5.6×10^4 g/mol, the number of entanglements per chain falls, as do the mechanical properties. Thus, the decrease in the number of entanglements per chain for high molecular weights in Packmol systems may contribute to the upper molecular weight limits.

Furthermore, the conformational properties were also calculated to explain the upper molecular weight limits. With an increase in molecular weight, both Packmol and Polyply models exhibit a trend of increasing end-to-end distance (Fig. 3a) and radius of gyration (Fig. 3b). However, for the systems built with Packmol, the end-to-end distance and radius of gyration begin to decline when the molecular weight exceeds 5.6×10^4 g/mol, where the mechanical properties of the models start to decrease. This also suggests that the molecular chains of higher molecular weight systems become more curled, which is not consistent with the conformation of the experimental polymer's random coil.^[79] A visual analysis of the models (as depicted in Figs. S4 and S5 in ESI and Figs. 3c and 3d) also reveal that, even after microseconds of equilibration, the molecular chains in Packmol model tend to curl up into clusters,

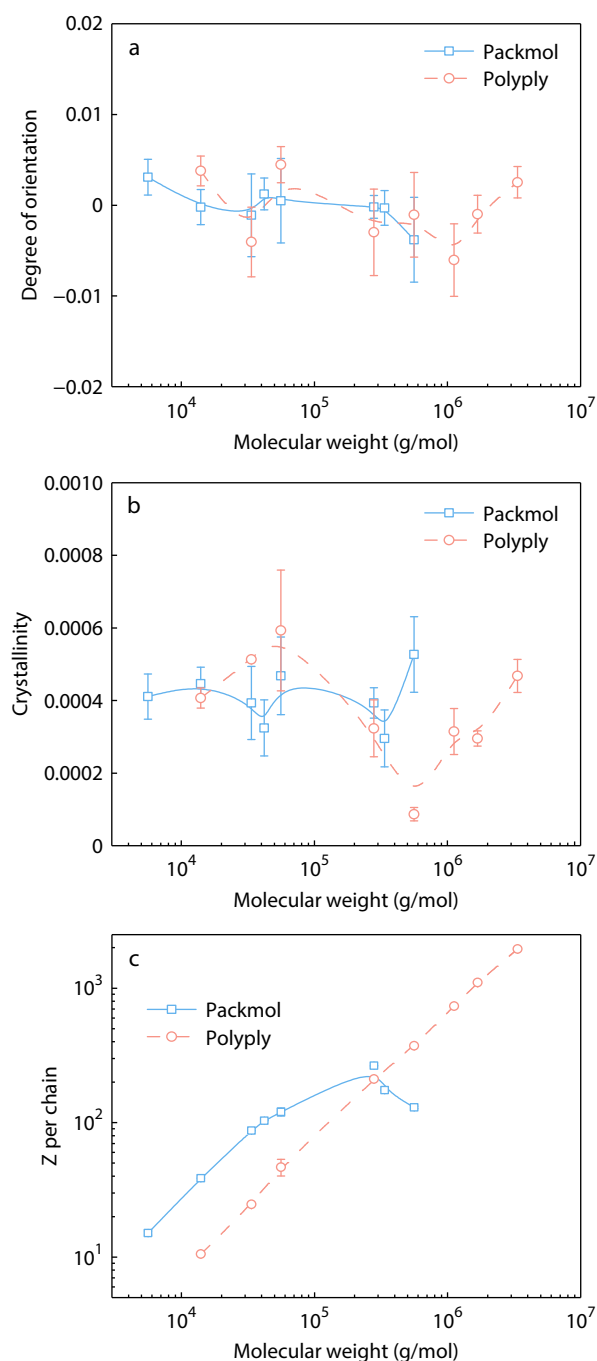


Fig. 2 The condensed state structure of PE models constructed using Packmol or Polyply, as a function of molecular weight: (a) the degree of orientation, (b) crystallinity and (c) the number of entanglements per chain (or Z per chain). The standard deviation of the datas in (c) are less than 10.

thereby inhibiting inter-chain entanglement and thus, the mechanical properties.

The potential cause of the Packmol modeling issue may be attributed to the equilibration procedure. For molecular chains with low molecular weight, the chains are so close to each other that they can interact and entangle during the subsequent equilibrium process, and the molecular chains essentially do not agglomerate separately. Therefore, the varia-

tion in end-to-end distance and radius of gyration is reasonable. For molecular chains with molecular weight higher than 5.6×10^4 g/mol, the spacing between the chains is too large after replicating the initial molecular chains, and in the subsequent equilibrium process, the molecular chains tend to curl into clusters before contacting with each other, resulting in the tendency of decreasing the end-to-end distance and radius of gyration. For models built with polyply, a random-walk algorithm was used to generate the coordinates of the beads, which ensures that the coordinates generated at each step do not overlap with those generated previously. Furthermore, Polyply adds a restraint mechanism to the random-walk protocol, allowing it to successfully enforce particular distance constraints between system residues. This results in a relatively straight path for the generated long molecular chains, which may cross the box multiple times. However, this method ultimately generates PE molecular chains in a random coil conformation and does not curl into clusters (Fig. S5i in ESI). As a result, the end-to-end distance and radius of gyration rise as molecular weight increases.

In the PE system modeled by Polyply, both the Young's modulus and breaking strength exhibit a declining trend once the molecular weight surpasses 5.6×10^5 g/mol, even though the number of entanglements per chain, end-to-end distance, and radius of gyration remain reasonable throughout the entire molecular weight range. However, when molecular weight reaches 5.6×10^5 g/mol, only 5–15 molecular chains were included in the simulation box, which differs significantly from the actual PE system. The limited number of molecular chains within the box may result in increased statistical errors. Moreover, complex entanglement can occur among polymer chains, significantly affecting the mechanical properties of the polymers. A small number of molecular chains hinders the formation of sufficient topological entanglement, making it difficult to accurately represent the behavior of real systems. Furthermore, the conformation and interactions of long-chain PE molecules are highly intricate. In simulations, it is essential to accurately describe the conformational changes, inter-chain interactions, and intra-chain interactions of the molecular chains. If these interaction descriptions are inaccurate or if important interactions are overlooked, it may ultimately result in deviations in the mechanical properties from experiment.

The PE models constructed with Packmol may not have reached equilibrium due to the initial chain conformation, particularly for long PE chains where entanglement is high. In contrast, Polyply employs a self-excluding random-walk algorithm, which is very similar to the Monte Carlo method. The coordinate generation at each step in this algorithm is based on a specific probability distribution that simulates thermal motion and conformational changes in real chains. As a result, the conformations of the final molecular chains generated by Polyply are near equilibrium, making it a more advisable tool for simulating long PE chains. Fig. S6 (in ESI) shows the energy, end-to-end distance and radius of gyration of PE models with a molecular weight of 5.6×10^5 g/mol, constructed with Polyply, during the final 400 ns of the equilibrium stage. After a long period of equilibrium, the energy, end-to-end distance, and radius of gyration of the Polyply models remain relatively constant. This suggests that models constructed with Polyply

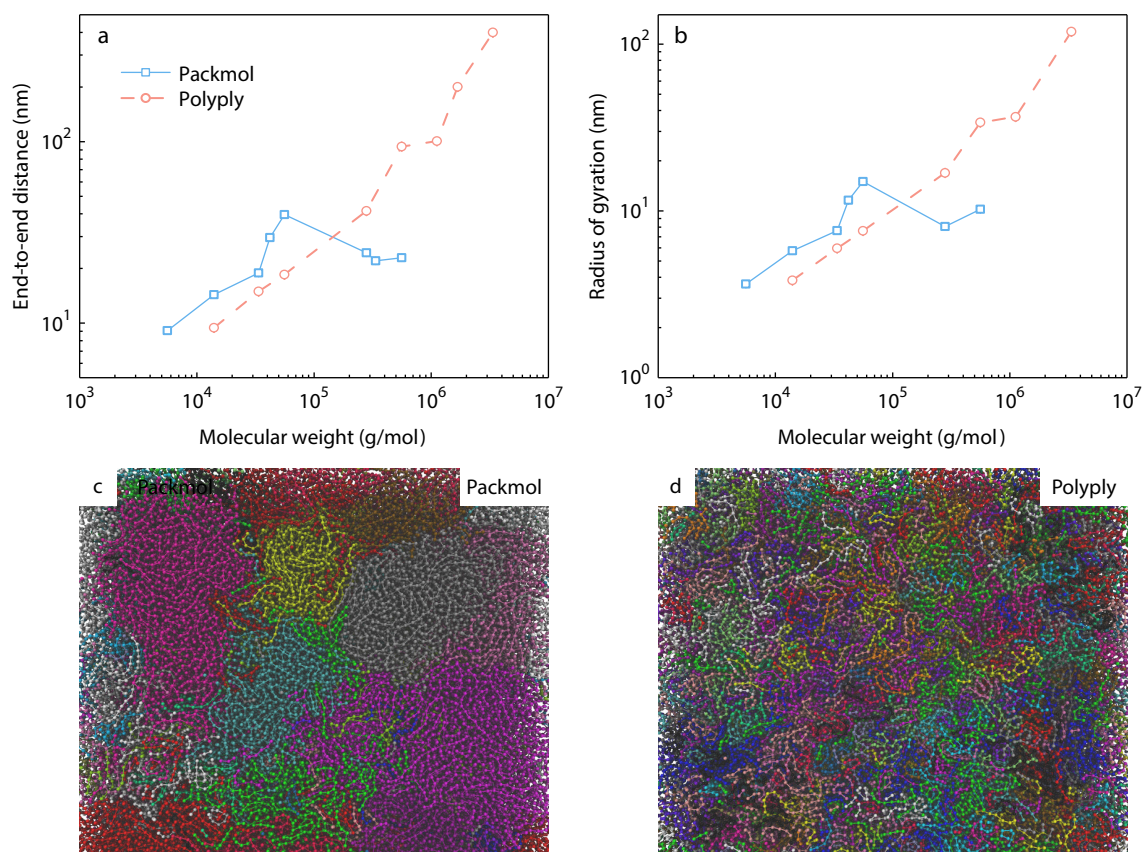


Fig. 3 The conformational properties of PE models constructed using Packmol or Polyply, as a function of molecular weight: (a) the end-to-end distance; (b) the radius of gyration. The standard deviation of the data in Fig. 3 are less than 0.05. Schematic representation for the representative PE models with a molecular weight of 5.6×10^5 g/mol: (c) Packmol, (d) Polyply.

have achieved equilibrium. The comparison between Packmol and Polyply is intended to illustrate how the initial structural setup impacts simulation results. While Packmol is a widely-used modeling tool in molecular dynamics, it has limitations when generating coordinates for very long chains. Our findings aim to serve as a cautionary reminder for other researchers to be mindful of these factors in future simulations.

In summary, Polyply-built systems display more reasonable mechanical behavior across a wider range of molecular weights compared to those built with Packmol. The molecular weights of these systems are closer to those of experimental UHMWPE, and their Young's modulus and breaking strength are similar to experimental UHMWPE. Therefore, Polyply-built systems serve as a good representation of UHMWPE. Additionally, it has been found that even after microseconds of equilibration, different initial structures can still influence the final conformational and mechanical properties of systems composed of long polymer chains (details are discussed in ESI). Caution is advised.

Factors Affecting the Mechanical Properties of PE Fibers

The hot stretching process of UHMWPE fibers is one of the important means to improve their performance. In industry, by hot stretching the fibers near the melting point of PE (390–410 K), the Young's modulus and breaking strength of the fibers can be further improved.^[80–82] To reproduce this process, we em-

ployed Polyply systems to perform tensile simulations on PE systems with molecular weights below 5.6×10^5 g/mol at 400 K, yielding fibers with different pre-elongation levels following cooling and equilibration for 10 μ s.

The stress variation with elongation during hot stretching is shown in the Fig. 4(a). During the hot-stretching procedure, the stress for PE models with varying molecular weights is kept low. When the pre-elongation (λ) reaches 6, there is a significant increase in stress, and the higher the molecular weight, the faster the rate of stress growth. The stress during the initial hot stretching process remained at approximately 5 MPa. This is attributed to the molecular chains being in a disordered state initially. After being stretched, these chains can alleviate the internal stress of the system through conformational changes and slippage between chains, thereby maintaining a lower stress level. Once the pre-elongation reaches 6, the increase in stress indicates that most of the molecular chains are oriented along the stretching direction, making it difficult for their conformation to transform. As a result, covalent bonds continuously endure increasing stress. Long-chain molecules can withstand higher stresses, which gives them a greater ultimate pre-elongation compared to short-chain molecules. After achieving the maximum re-elongation, a huge number of defects occurred within the PE models, resulting in fiber breaking.

The fibers were subsequently stretched along the fiber axis at a tensile rate of 0.005 nm/ps at 300K and the stress-strain

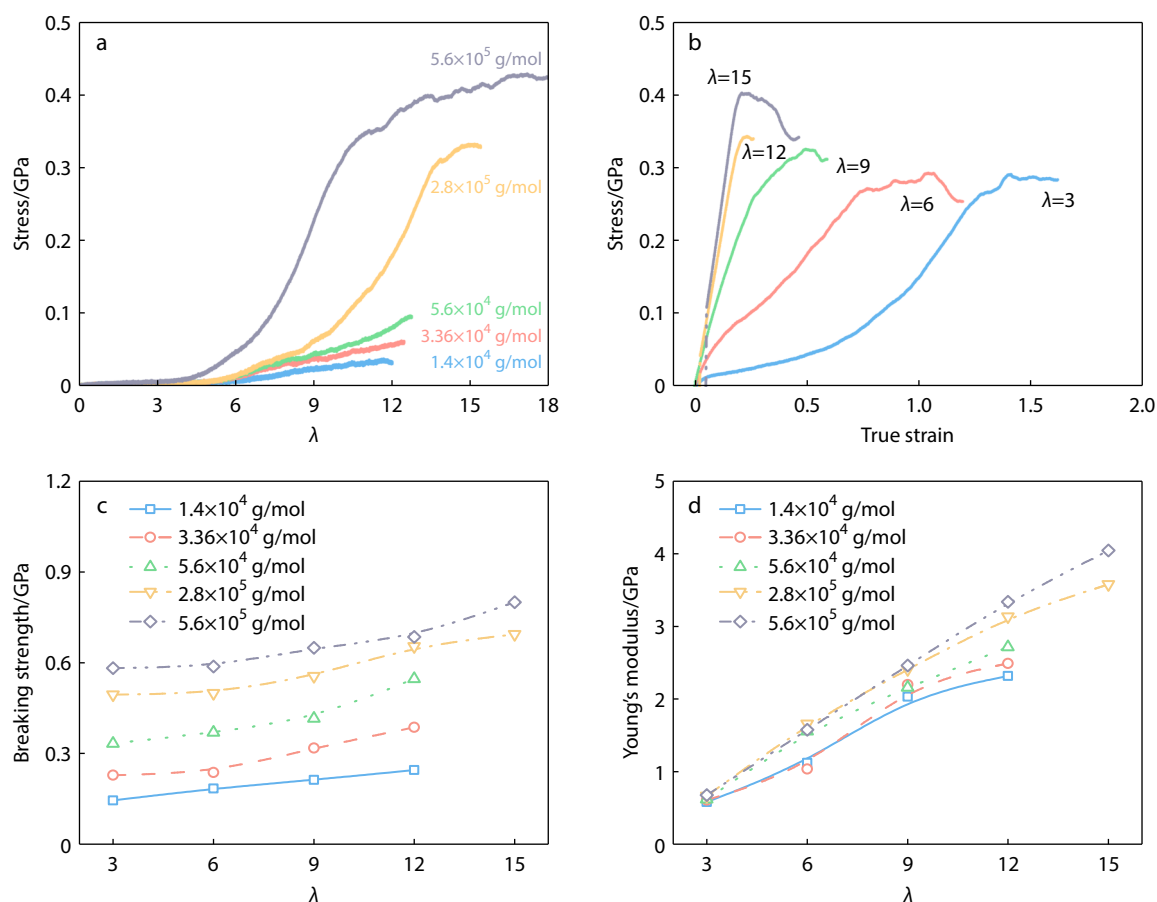


Fig. 4 (a) The stress variation with pre-elongation (λ) during hot stretching; (b) Stress-strain curves of PE fibers with a molecular weight of 5.6×10^5 g/mol; (c) Young's modulus and (d) breaking strength of PE fibers of different molecular weights, as a function of pre-elongation.

curves of the fibers are illustrated in Fig. S7 (in ESI). Take 5.6×10^5 g/mol molecular weight PE fibers as examples for analysis. The true stress-strain curves of fibers with different pre-elongation show different characteristics (Fig. 4b). The fibers with lower elongations initially undergo elastic deformation, followed by entering the stage of strain development. The curves rise sharply before fracture, indicating that the fibers undergo a strain-hardening phase, and finally the fiber breaks. This suggests that the lower pre-elongation ($\lambda < 6$) PE systems exhibit a rubbery state due to its lower crystallinity and degree of orientation. In contrast, PE systems with higher pre-elongation ($\lambda > 9$) undergo only elastic deformation before fracture. These phenomena at both low and high pre-elongations align with the stress-strain curve observed in the experiment of UHMWPE fibers.^[82,83] The Young's modulus and breaking strength of fibers with different molecular weights were calculated as a function of pre-elongation (Figs. 4c and 4d). Higher molecular weight fibers exhibit higher Young's modulus and breaking strength. Besides, higher molecular weight PE systems can achieve greater pre-elongation, resulting in PE fibers with enhanced Young's modulus and breaking strength. The maximum pre-elongation achieved by simulating fibers align with theoretical laws and experimental results.^[70,84,85] The elongation at break of the simulated fibers decreases as the stretching ratio increases (Fig. S7f in ESI). Even though the absolute values obtained

from the simulation differ from the experimental data, they generally align with the elongation at break reported in other simulations.^[19,24,25,41] Furthermore, this trend is consistent with findings from experiments.

To explore the mechanisms behind the varied mechanical properties of fibers, the condensed-state structure parameters such as orientation, crystallinity, and entanglement of the fibers were computed. As the pre-elongation increases, the degree of orientation and crystallinity of the fibers increase, while the number of entanglements decreases (Fig. S8 in ESI). Fig. 5 illustrates the distribution of PE fibers in their crystalline states as their pre-elongation varies. With higher pre-elongation, the crystallization area expands and crystallinity improves. Therefore, as the pre-elongation increases, PE polymer adopts a more ordered arrangement, forming a more crystalline structure with fewer entanglements. Noted that across various molecular weights of PE fibers, the degree of orientation remains nearly constant at the same pre-elongation, suggesting that molecular weight does not directly impact fiber orientation. Instead, the crystallinity and the degree of entanglement at the same pre-elongation varies for different molecular weights of PE fibers.

The increased orientation and crystallinity of the fibers could lead to the observed upward trend in Young's modulus (Figs. 6a and 6b), which is consistent with the phenomenon reported in the experiment.^[82,86,87] This is because that the

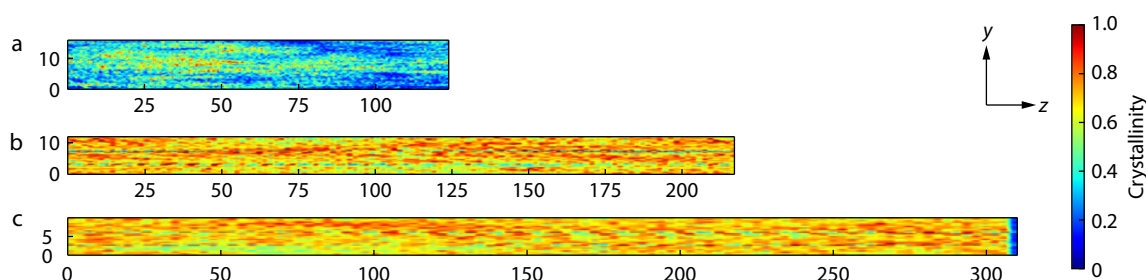


Fig. 5 Schematic representation for the PE fibers in crystalline states: (a) $\lambda=3$; (b) $\lambda=6$; (c) $\lambda=9$.

process of hot-stretching promotes fiber orientation, which in turn leads to crystallization. An increase in orientation and crystallinity implies a more regular macromolecular structure within the fiber, facilitating the formation of a more efficient stress transfer pathway. When an external force is applied to the fiber, a highly oriented crystalline fiber can more effectively distribute the stress across each macromolecule and resist axial deformation, so the Young's modulus basically increases monotonically with the degree of orientation and crystallinity.^[88] Thus, even low molecular weight fibers with high orientation and crystallinity can exhibit higher Young's modulus than high molecular weight fibers with low orientation and crystallinity.

For fibers with the same molecular weight, as the number of entanglements per chain decreases, the Young's modulus of the fibers increase (Fig. 6c). Despite fewer entanglements, the highly oriented and organized structure can effectively withstand external deformation, thereby enhancing the Young's modulus. Therefore, it can be considered that the influence of the number of entanglements per chain on Young's modulus is weaker than that of the degree of orientation and crystallinity for our PE fiber system.

For the breaking strength of the fibers, it can be inferred that the breaking strength is mainly affected by molecular weight of fibers (Figs. 6d–6f). For low molecular weight fibers, even with high orientation and crystallinity, the breaking strength is lower than that of high molecular weight fibers with low orientation and crystallinity. This is because there are more chain ends in low molecular weight fiber systems, which can easily cause structural defects in the fibers and may become the starting point for microcrack formation, which may reduce the breaking strength of the fibers. This indicates that increasing the molecular weight of PE to obtain higher elongation fibers is the key means to obtain PE fibers with higher breaking strength.

For PE fibers of the same molecular weight, increasing orientation degree and crystallinity, along with a decrease in the number of chain entanglements, leads to higher breaking strength. Similar to the effect on Young's modulus, the ordered arrangement can also increase the breaking strength.

For high molecular weight PE systems, the length of the molecular chain is significantly greater than the dimensions of the simulation box. This setup can lead to finite size effects, which may influence the mechanical properties of the system. Many researchers have explored the impact of box size on the diffusion coefficient,^[89,90] crystallization rate,^[91,92] and entanglements^[93] by constructing models of varying box sizes. Yeh et al.^[50] quantified the finite size effect by conducting tensile

simulations on semi-crystalline PE models of different sizes and comparing the overall characteristics of the stress-strain curves. To determine the influence of finite size effects on the mechanical properties of simulated PE fibers, we constructed tensile simulations at 400 K on a larger model box (40 nm × 40 nm × 40 nm) with different molecular weight and compared it with the previous model (32 nm × 32 nm × 32 nm). As shown in Fig. S9 (in ESI), for systems with lower molecular weights ($\leq 5.6 \times 10^4$ g/mol), the stress-strain curves exhibit minimal deviation, implying that the box size has a negligible impact on the results. Conversely, for high molecular weight systems ($\geq 3.36 \times 10^5$ g/mol), when λ surpasses the value of 6, marked disparities become evident in the stress-strain curves among systems with differing box sizes. This observation underscores the presence of pronounced finite size effects within these high molecular weight systems, the mechanical properties may exhibit considerable deviations. Furthermore, we measured the Young's modulus and breaking strength of high molecular weight systems at 300 K (see Figs. S9b and S9c in ESI). It is evident that fibers with different box sizes exhibit significant variations in Young's modulus and breaking strength; however, the Young's modulus and breaking strength of fibers increase with rising molecular weight, which is still consistent with the experimental results. The finite size effect does influence the actual values of the simulated mechanical properties of PE fibers in our system; however, it does not alter the overall trend of changes in these properties. Therefore, our subsequent analysis and machine learning calculations regarding the contributions of the three factors remain valid.

To explain the breaking behavior of PE fibers, the energy of the PE systems during tensile simulation of fibers with different pre-elongation at 300 K is decomposed into bonding energy, angular energy, dihedral energy, and non-bonding interaction energy (Figs. S10–S14 in ESI). Take 1.4×10^4 g/mol molecular weight PE fibers as examples, the energy changes during fiber stretching are investigated. For fibers with low pre-elongation ($\lambda < 3$) (Fig. S10a in ESI), the dihedral and angular energies change considerably at the beginning of stretching, whereas the bond energy, non-bonding interaction energy, and total potential energy remain almost constant. This is due to the lower degree of orientation of the fibers, the conformational change of the molecular chains under external forces, and the dissipation of energy through the angles and rotation of the dihedral to accommodate the deformation. While for the fibers with high pre-elongation ($\lambda > 6$) (Figs. S10b–10d), the changes of dihedral and angular energies are minimal. This is due to their high degree of initial orientation and crystallization (Figs. 6a and 6b), which limits conforma-

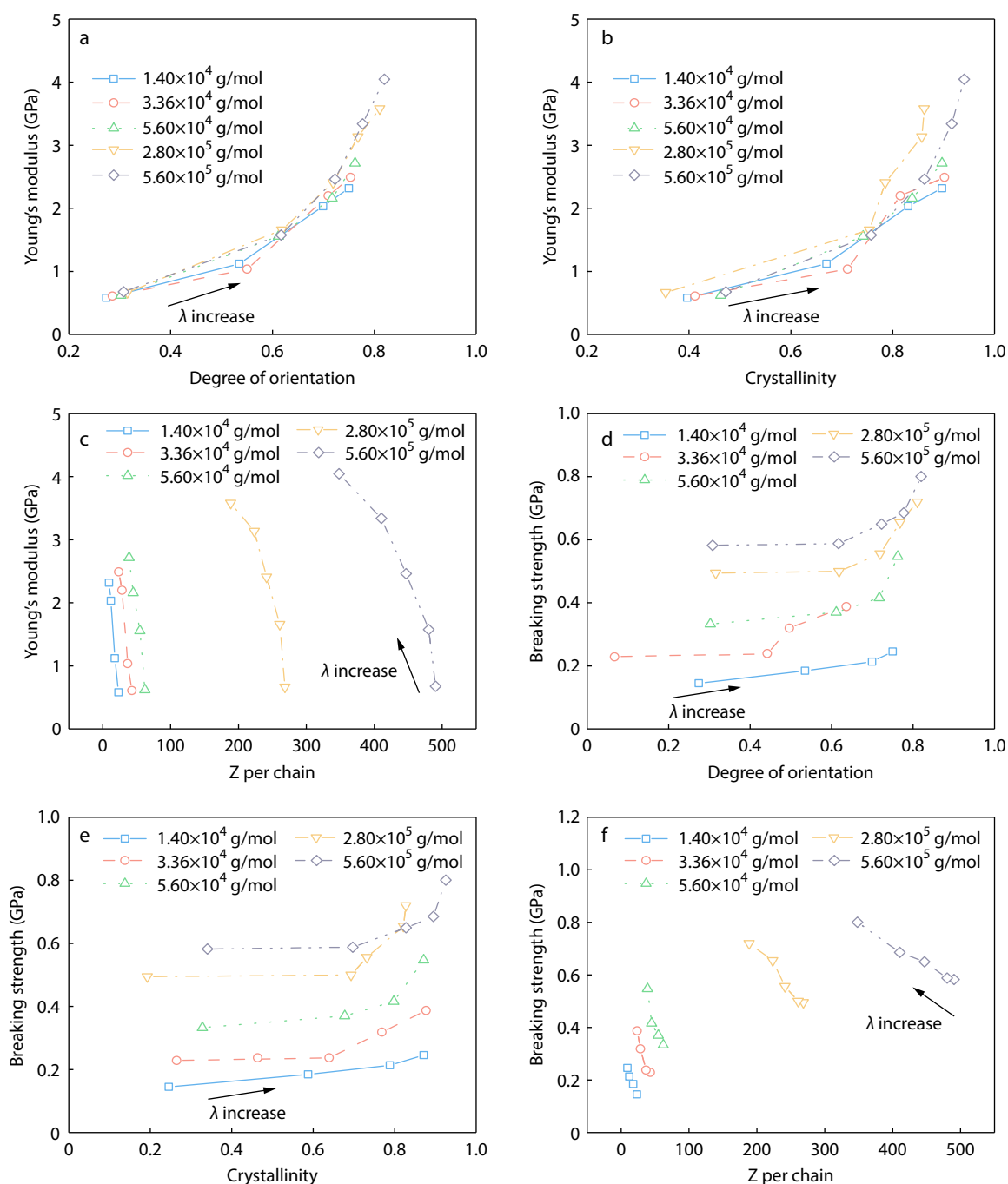


Fig. 6 The Young's modulus of PE fibers with different molecular weights, as a function of (a) the degree of orientation, (b) the crystallinity and (c) the number of entanglements per chain; The breaking strength of PE fibers of different molecular weights, as a function of (d) the degree of orientation, (e) the crystallinity and (f) the number of entanglements per chain.

tional transitions, resulting in more stable conformations.

In general, the potential energy of PE fibers gradually increases during stretching. The change in potential energy from stretching to breaking indicates the amount of energy the fibers can withstand. As the molecular weight of PE fibers increases, the bond energy significantly rises, leading to a higher total potential energy required for fiber breakage, while the changes in angle and dihedral energy are less significant (Fig. 7). This indicates that longer molecular chains allow the covalent bonds of PE fibers to contribute more in re-

sisting the external stretching force, making it relatively difficult for the molecular chains to disentangle and slip, ultimately significantly increasing the total potential energy required for fiber breakage. Meanwhile, increased pre-elongation plays a vital role in enhancing fiber bond energy and total potential energy. Higher molecular chains are required to generate fibers with higher pre-elongations, hence we assume that molecular weight has the greatest contribution to fracture strength. The results of energy decomposition further demonstrate the significant contribution of molecular weight

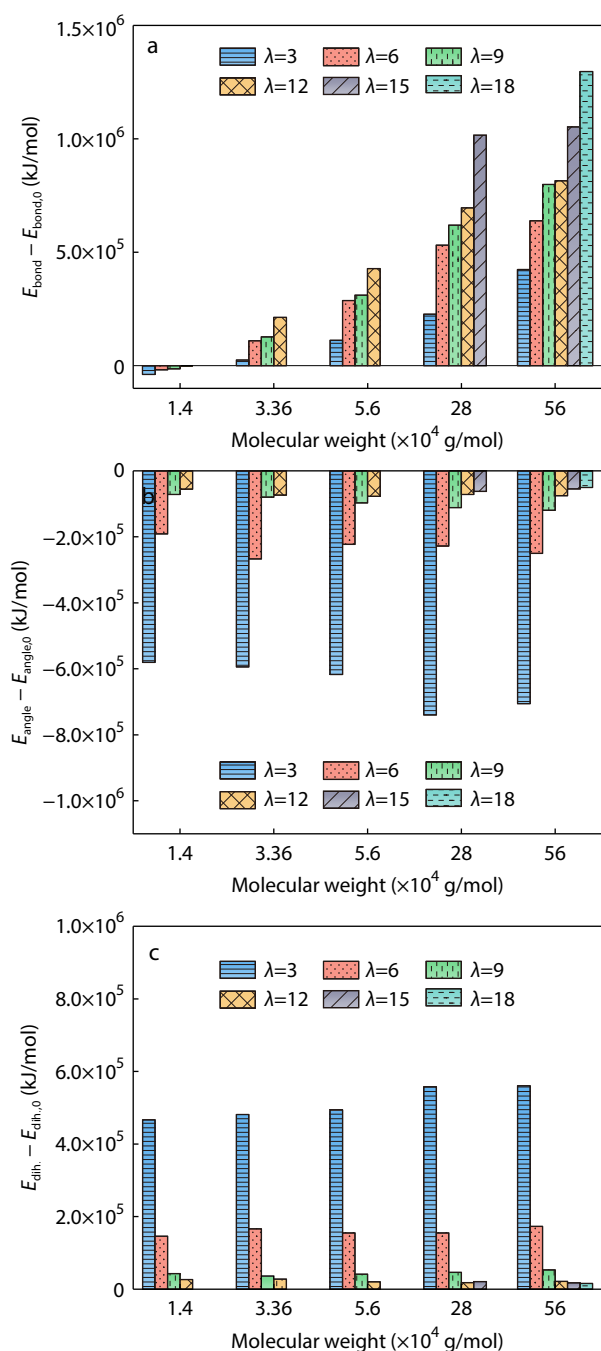


Fig. 7 The change of potential energy during the tensile simulation. (a) Bond energy before fiber breaking minus initial bond energy for fibers of different molecular weights; (b) Angle energy before fiber breaking minus initial angle energy for fibers of different molecular weights; (c) Dihedral energy before fiber breaking minus initial dihedral energy for fibers of different molecular weights.

to fiber breaking strength, which is consistent with the conclusion of the tension simulations.

Machine Learning of Mechanical Properties of PE Fibers

We aim to calculate the percentage contribution of three factors to the mechanical properties of fibers based on simulated

data. However, due to the multicollinearity of orientation and crystallinity in the dataset, the least squares algorithm cannot find a unique and reasonable solution. The issue of multicollinearity can typically be addressed by manually removing certain features; however, these features significantly influence the mechanical properties of fibers and are indispensable, especially in the industrial sector. Therefore, we employed both linear and nonlinear machine learning algorithms to predict the mechanical properties of fibers based on these three key factors, and contributions from these factors were quantified as well. However, prior to conducting the machine learning analysis, we were uncertain which algorithm would perform better (linear, nonlinear or any complicated form). Therefore, we needed to utilize various machine learning techniques to identify the optimal approach.

Machine learning involves analyzing input data sets with various algorithms to uncover intrinsic patterns and create a mathematical model. This model can then be used to make predictions or decisions about new, similar data. By applying machine learning to build models from molecular dynamics (MD) simulation data and deriving empirical formulas, we can calculate the percentage contribution of each factor to the mechanical properties based on the coefficients in these formulas. This approach enables a quantitative assessment of how different structural factors affect the mechanical properties of polyethylene fibers. Here, Linear, Ridge, Lasso, Elastic Net, Voting, Stacking, Polynomial, XGBoost, Tree, Random Forest and Neural Network regression techniques in machine learning were employed to explore the relative importance of structure parameters such as molecular weight, orientation, and crystallinity in determining the Young's modulus and breaking strength of PE fibers.

To choose the best algorithm, the coefficient of determination and root mean square deviation of the test set (Fig. 8) are measures to evaluate the performance of the fitted regression model. The closer the R^2 is to 1, the closer the RMSE is to 0, indicating that the fitted model is better behaved.

We employ a variety of machine learning algorithms, including both traditional linear and nonlinear methods, as well as deep learning techniques, to identify models with high R^2 values. For models labeled with Young's modulus, the R^2 value in traditional linear machine learning is approximately 70%. In contrast, the R^2 values for nonlinear models, such as random forest regression and deep neural networks, are 93.4% and 97.5%, respectively. Similarly, for models labeled with breaking strength, neural networks achieve the highest R^2 value of 95%. Compared to multi-layer perceptrons (MLPs), which can only fit linear classifiers, neural networks utilize various nonlinear activation functions—such as ReLU, sigmoid, or tanh—to learn complex nonlinear decision boundaries. This capability allows them to overcome the limitations of linear classifiers. Consequently, by selecting an appropriate activation function, neural networks can theoretically approximate and fit any function, allowing them to capture complex nonlinear relationships among three feature values, thereby enhancing the accuracy of regression analysis. Additionally, neural networks can progressively learn to recognize patterns in data through their self-learning capabilities. This adaptability enables them to continuously optimize their performance when addressing regression problems, ultimately

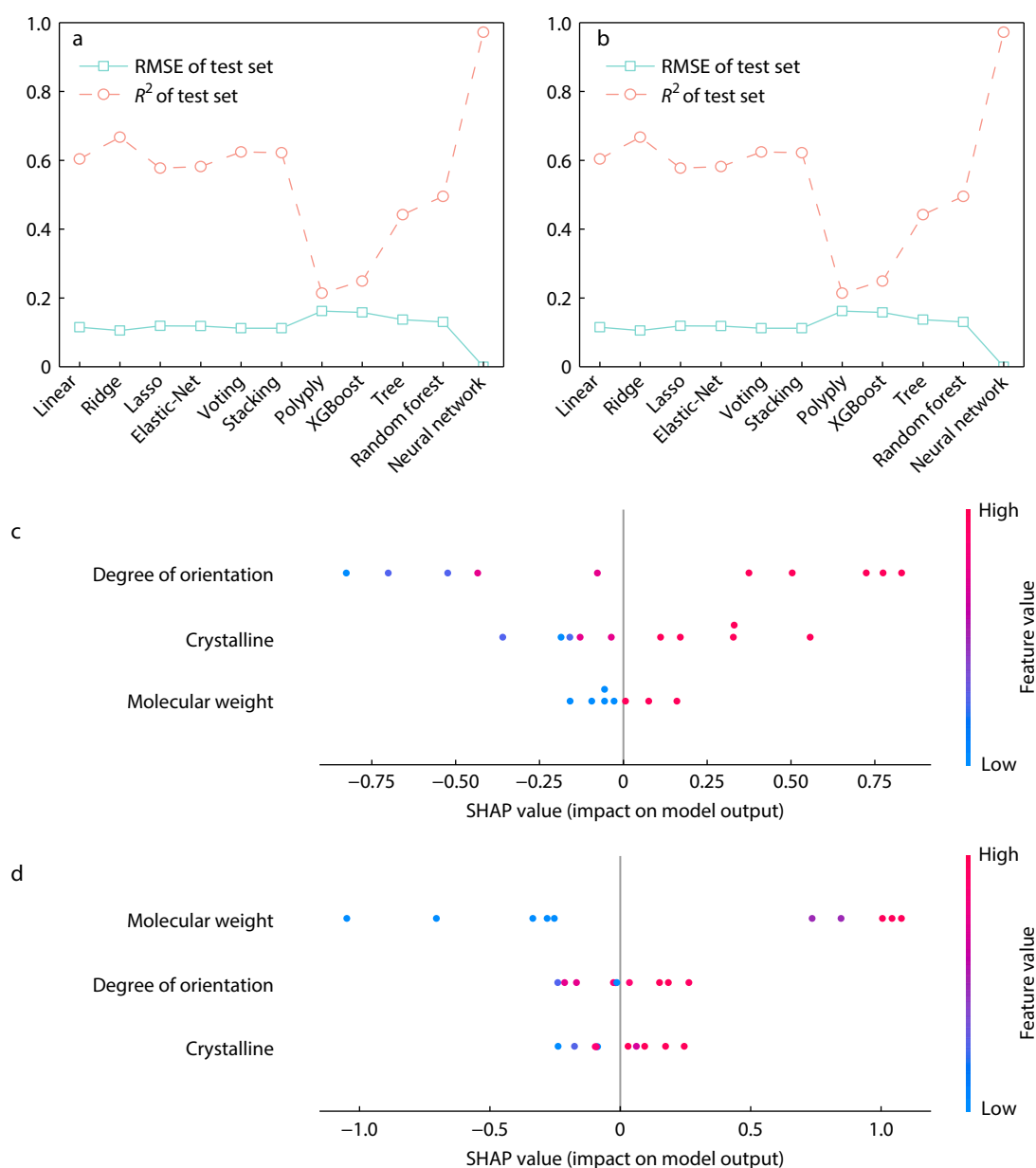


Fig. 8 (a) The determination coefficient (R^2) and root mean square deviation error (RMSE) of regression model, using simulated Young's modulus as the label; (b) R^2 and RMSE of regression model, using simulated breaking strength as the label; (c) The bee swarm plot of neural network regression model, using simulated Young's modulus as the label; (d) The bee swarm plot of neural network regression model, using simulated breaking strength as the label.

achieving higher R^2 values. However, neural networks often lack transparency, making it difficult to discern the relative importance of different features. To address this, we calculate SHAP (SHapley Additive exPlanations) values to assess the impact of three different factors on mechanical properties. We sum the absolute SHAP values of each feature and determine the proportion of each feature's sum relative to the total sum of all features, as illustrated in Figs. 8(c) and 8(d). The degree of orientation has the highest contribution (60%) to the Young's modulus of PE fibers, followed by the crystallinity (26%), and the molecular weight contribution is the lowest (14%). The contribution of molecular weight to the breaking strength of PE fibers is the highest (65%), followed by orienta-

tion (29%), and the contribution of crystallinity is the lowest (6%).

This means that to increase the Young's modulus of PE fibers, more emphasis should be placed on improving the degree of orientation and crystallinity of the fibers. Young's modulus is a physical quantity that measures the stiffness of an object, which is related to fibers' internal molecular structure. Achieving full extension and parallel arrangement of each molecular chain in the fiber can improve the degree of orientation of the fiber. The highly oriented and crystalline fiber can more effectively distribute the stress across each macromolecule and resist axial deformation, resulting in an enhancement in fiber stiffness. The molecular chains of PE

fibers with lower molecular weight are more easily stretched to achieve parallel arrangement of chain segments (Fig. 9a), exhibiting a high Young's modulus comparable to that of high molecular weight PE fibers.^[94] Therefore, the key to increase the Young's modulus of fibers in industry is to improve the orientation of the fibers.

The contribution of molecular weight to the breaking strength of fibers is the highest. Because the fracture of low molecular weight fibers is mainly caused by the disruption of non-bonding interactions, leading to the disentanglement and slippage of molecular chains (Fig. 9a). When high molecular weight fibers are stretched (Fig. 9b), covalent bonds participate in the process of resisting external deformation, so higher molecular weight fibers require more energy to break (Fig. 7a). In addition, low molecular weight fiber structures have more chain ends inside, which can easily lead to defects in the fibers.^[95,96] Under external forces, non-bonding interactions at the end of the chain are more easily disrupted, and even with higher crystallinity and orientation, the breaking strength of the fiber cannot be improved. The significant impact of molecular weight on breaking strength implies that achieving high-strength UHMWPE fibers necessitates higher molecular weight PE materials. Additionally, the contribution of crystallinity and orientation should not be neglected, as they are also important factors affecting the fiber breaking strength.

Overall, the Young's modulus and breaking strength of PE fibers increase with the increase of molecular weight, the degree of orientation and crystallinity, but the contribution of different structural factors to the modulus and strength varies. The increase in the degree of orientation and crystallinity makes the fiber more effective in resisting external deformation, thereby significantly improving the Young's modulus of the fiber. And the reduction of internal chain end defects in higher molecular weight fibers requires higher energy to break, thus significantly improving the fiber breaking strength.

In industrial production, three key indicators—molecular weight, degree of orientation, and crystallinity—can be directly measured. However, these three factors are interrelated, making it challenging to isolate their individual impacts on mechanical properties. We utilize machine learning to identify the optimal regression model that maximizes the R^2 value. Concurrently, we calculate the SHAP values for three

features and assess their percentage contributions of these factors to the mechanical properties of the fibers. Our work is highly significant in quantifying the impact of three factors and providing guidance for industrial production. Researchers should prioritize enhancing the factor with the largest contribution, as this approach is likely to facilitate breakthroughs in the mechanical properties of fibers. This focus is essential for producing UHMWPE fibers with greater strength and modulus for future industrial applications.

There have been numerous studies on the stress response of molecular chains in semi-crystalline PE under uniaxial tension.^[40,50,55,97] During uniaxial tensile deformation, the PE melt experiences entanglement loss, chain rearrangement, and crystal nucleation, with significant void formation observed at high strain levels.^[38] The extension and orientation of the chain segments during the stretching process reduce the barriers to primary nucleation, enabling researchers to observe the nucleation and growth of PE crystals within the time frame of molecular dynamics simulations. Furthermore, the crystallization of PE under uniaxial tension is a function of total strain and the strain rate.^[29] The response of PE molecular chains to stress, as observed in our study, aligns with the findings of previous researches.^[41,98] However, in our study, we examined PE models with higher molecular weights compared to previous researches. It can be observed that, under the same strain, models with greater molecular weights exhibit increased internal stress and can achieve higher tensile ratios. The model with elevated stretching ratios is more representative of the ultra-high molecular weight polyethylene fibers used in the experiment.

Numerous studies have been conducted on the primary deformation mechanisms of PE during uniaxial tensile loading.^[19,29,39,99] Amorphous PE initially exhibit an elastic response under low-temperature stretching, followed by a yield peak, softening, strain hardening, and ultimately fracture. In contrast, high-crystallinity PE fibers display only linear and elastic stress-strain behavior. Our research not only reproduce these two typical stress responses but, more importantly, provides an analysis of the contributions to the tensile properties of PE fibers with varying molecular weights and condensed structures. Through energy decomposition and machine learning techniques, we discovered that the three structural characteristics of the fibers significantly influence their Young's modulus and breaking strength to varying de-

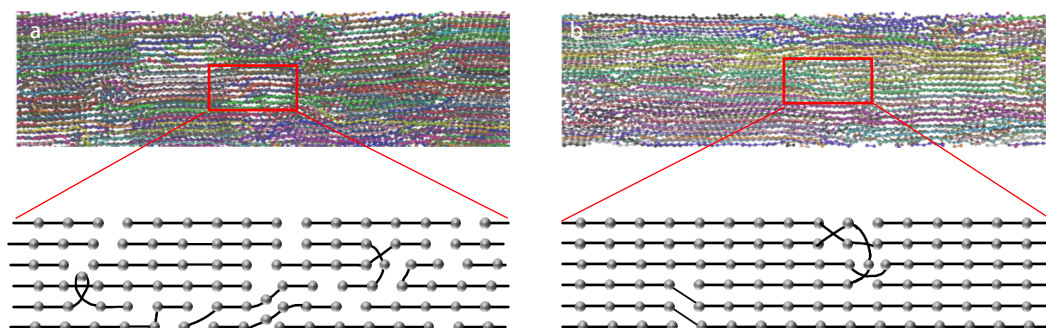


Fig. 9 (a) Schematic diagram of the stretching process of low molecular weight PE fibers with more chain ends; (b) Schematic diagram of the stretching process of high molecular weight PE fibers with fewer chain ends and the covalent bonds involved participate in the process of resisting external deformation.

grees. Quantifying the percentage contributions of these three factors to the mechanical properties of the fibers is crucial for future research on the relationship between polymer structure and properties. In the future, we should strive to simulate PE fibers with higher molecular weights and further investigate how various crystal morphologies within the fibers affect their mechanical properties. This research will provide more valuable insights for fiber processing in the industry.

CONCLUSIONS

Martini molecular dynamics simulations were employed to study the structure and mechanical property of semi-crystalline PE fibers with varying molecular weights. The systems built with Polyply exhibit reasonable conformation and mechanical properties. By comparing the Young's modulus and breaking strength of Polyply-built systems with experimental UHMWPE data, it is believed that these systems can accurately represent UHMWPE as observed in experiments. Therefore, the Polyply-built systems was chosen for uniaxial stretching to produce PE fibers with different pre-elongations. After the pre-elongation of the fiber exceeds 6, the stress increases significantly. At this stage, the molecular chains exhibit a relatively complete orientation structure. The subsequent low-temperature cooling process stabilizes the fiber's structure, resulting in highly oriented and crystalline fibers. Despite the influence of finite size effects on certain high molecular weight fiber models, the observed trends in their mechanical properties remain in agreement with experimental findings. The results of MD simulation indicate that the Young's modulus is mainly affected by the degree of orientation and crystallinity. However, the energy decomposition suggests that molecular weight plays a more crucial role in the breaking strength. As molecular weight increases, covalent bonds within the fiber can endure greater energy during stretching, leading to a higher energy requirement for fiber breakage. What's more, machine learning was utilized to calculate the percentage contribution of molecular weight, the degree of orientation and crystallinity to Young's modulus and breaking strength. The calculations show that degree of orientation had the most significant contribution to the Young's modulus of PE fibers (60%), followed by the crystallinity (26%), with molecular weight contributing the least (14%). Conversely, molecular weight had the highest contribution to the breaking strength of PE fibers (65%), followed by degree of orientation (29%), with the crystallinity contributing the least (6%). Clarifying the extent to which the three factors contribute to the mechanical properties of the fibers helps us identify the key to enhancing the performance of UHMWPE fibers.

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/>

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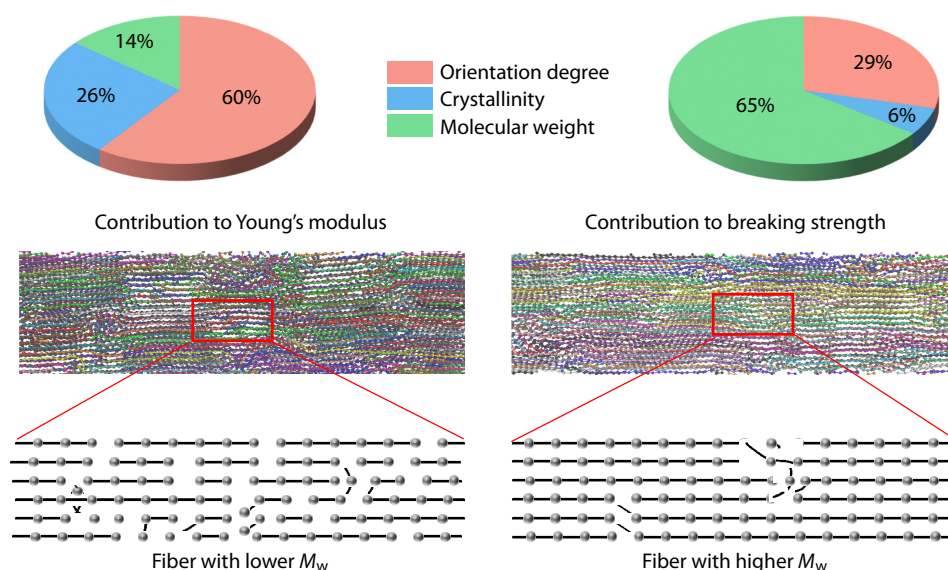
Graphical Abstract

Simulation of the Specific Contributions of Molecular Weight, Orientation Degree, and Crystallinity to the Tensile Mechanics of Polyethylene Fibers

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A reasonable model of UHMWPE fiber was constructed using PolyPy. By integrating molecular dynamics simulations with machine learning, it was found that orientation contributed most to the Young's modulus, accounting for 60%, while molecular weight played the most critical role in determining the breaking strength, accounting for 65%.



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