Molecular Dynamics Study of Poly(dimethylsiloxane) Nanostructure Distortion in a Soft Lithography Demolding Process

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ABSTRACT: This study aims at investigating the distortion of poly(dimethylsiloxane) (PDMS) nanostructures in a soft lithography demolding process using molecular dynamics simulation. Experimental results show that after peeling, PDMS nanopillars became 10−60% longer in height than the mold size. Molecular dynamics simulations have been employed to plot the stress–strain curve of the nanopillars when subjected to uniaxial stress. Three force fields (COMPASS, CVFF, and PCFF) were used for modeling. The demolding process in soft lithography and nanoimprint lithography causes significant deformation in replication. The experimental results show clear signs of elongation after demolding. Molecular dynamics simulations are employed to study the stress–strain relationship of the PDMS nanopillars. The results from the simulation show that a PDMS nanopillar at temperature \( T = 300 \text{ K} \) under tensile stress shows characteristics of flexible plastic under tensile stress and has a lower Young’s modulus, ultimate tensile stress, and Poisson’s ratio.

INTRODUCTION
Nanoimprint lithography (NIL) was first introduced by Chou et al. in 1995 and has shown promising potential to produce low-cost, high-resolution, high-throughput continuous nanostructures. NIL uses the simple concept of material displacement by mechanical contact as shown in Figure 1. This method enables continuous pattern transfer from a mold to a target substrate. While the concept is simple, many factors may cause distortion in the replications, such as temperature, pressure, aspect ratio, peeling-off technique, etc. Thus, when all distortion factors are accumulated, it is key in the manufacturing process to understand the stress and strain relationship of a substrate in the demolding process (Figure 2).

Figures 3 and 4 show the experimental results for the fabricated mold dimension and replication dimension, respectively. The experimental results obtained show that the height of the PDMS replication increased 30−65% from the depth obtained from the master mold. This information is crucial for NIL, because the entire concept of NIL is to obtain exact replica from continuous press and peel-off of mold to plastic. Figure 2 illustrates the elongation of PDMS replica during the demolding process.

The results from experiment set an objective for this study to investigate the stress and strain relationship of PDMS nanostructures. However, a major challenge for nanoscale materials is that there are no standardized and well-assessed equipment or methodology for stress–strain experimental studies. Although new tools have been developed to study mechanical properties on the nanoscale experimentally, the results are not always reliable. For example, the only experimental data for Young’s Modulus of nanostructures are mostly derived from the bending and nanoindentation test. A proper experimental data from uniaxial tension cannot be obtained because of the limitation to obtain a completely freestanding sample.

Hence, this study has employed the molecular dynamics (MD) method to investigate the PDMS distortion nanostructure in the demolding process. The MD method has helped engineers and scientists in complex problems relating to microelectromechanical systems (MEMS) research. In this study, MD was used to study the stress–strain relationship of PDMS nanostructures when subject to uniaxial stress.

RESULTS AND DISCUSSION
The equilibrium process i.e., NVT and NPT, and loading simulations are conducted at a temperature of 300 K and a pressure of 1 atm. While many studies of uniaxial loading are at a temperature lower than room temperature, most of the soft lithography and NIL processes are performed at room temperature or higher. Thus, simulation results show a significant thermal effect on the stress–strain curve. A previous study has shown that the structure and dynamics of PDMS at a temperature of 500K relaxed to 300 K is in the form of melt although bulk PDMS is solid at a temperature of 300 K. The
study shows the tremendous effects of heat on a polymer at the nanoscale.\textsuperscript{16–18} Combining a small strain rate and thermal effect, the result obtained in this study shows that the PDMS nanostructure show noticeably ductile material behavior. Figure 5 shows the uniaxial deformation of PDMS at strains of (a) 0.0, (b) 0.1, and (c) 0.3 via constant strain along the x-axis in the periodic simulation cell. This study used a small strain rate $\dot{\epsilon} = 0.01\% \text{ fs}^{-1}$, for the system to relax at every timestep.\textsuperscript{19,20} This in return minimizes crazing, which is typically observed in linear polymer glass at high strain.\textsuperscript{21} However, it is important to note that when a cavity is formed, it is impossible to relax and undo the cavity while the system is under strain. Visual inspection show that a cavity formed at a certain point for sufficiently high stress as illustrated in Figure 5c. When cavity takes form, the strain energy relieved is balanced by the surface energy of the newly generated surfaces.\textsuperscript{22} The study shows that when stress is applied beyond the point of cavity formation, the polymer chain will become elongated and ordered and eventually facilitate fibril formation.\textsuperscript{16}

The study found that cavity formation is a highly localized process in which the monomer around the cavity does not move very much.\textsuperscript{16} Our inspection revealed that the cavity
formed at certain points for the eight-monomer series is about the same as that for the 12-monomer series. This is because the cohesive energy, i.e., the nonbonded interaction of PDMS for both series, is about the same. Cavity formation might differ if the chain length was set to be longer as the influence of the chain length has been proved to have a significant effect on mechanical properties. A study by Lavine et al. showed that polyethylene with alkane chain C > 100 has significant resistance to reorientation of the molecules due to entanglement. For PDMS, the alignment of the two CH₃ groups is an important factor for determining the entanglement length. Thus, varying the chain length to longer series and studying the entanglement by looking at the isolated chain might have proved important. Future work will include simulation of PDMS under tension with a greater range of chain lengths.

Figures 6–8 show the stress–strain behavior of the PDMS eight-series and 12-series monomer nanopillars simulated at T = 300 K and \( \dot{\varepsilon} = 0.01\% \) s⁻¹ from the initial state to complete rupture. Although the strain used is high, such a strain rate has been used in impact-induced deformation. It is noted that the strain used is not comparable to experimental observations provided in the Introduction Section. The observations were used as a lead in this study.

The force field used in the simulation in Figures 6–8 is Condensed-phase optimized molecular potentials for atomic simulation studies (COMPASS) force field, consistent valence force field (CVFF), and polymer consistent force field (PCFF), respectively. For bulk PDMS, the normal stress–strain curve exhibits a general elastomer pattern. However, for this study, the stress–strain curve obtained exhibits a flexible plastic pattern with significant yielding. This kind of behavior occurs in nanostructures under tension due to the thermal effect as mentioned earlier. The extension of PDMS nanopillars started with elastic deformation from its initial state to the first yielding represented by the dot-dashed line in the graph. The results show that for all force fields, the 12-monomer series has slightly higher stress for any strain than the eight-monomer series. This result is expected because longer chains have longer entanglement lengths. More energy is also needed for longer polymer chains to elongate and reorder. In our result, the PDMS nanopillars ruptured at strains of 0.8, 0.7, and 0.8 for COMPASS, CVFF, and PCFF, respectively. This is slightly lower than bulk PDMS at a strain of 1.0. This is expected because thickness significantly affects tensile strength.

After the stress–strain reaches the ultimate tensile stress, there is a steady drop until rupture. This indicates structural changes and atomic reconstructing and reordering. Several studies reported that when the polymer is under stress, the polymer chains will be elongated and ordered and, subsequently, site nucleation and the growth of the crystalline phase are observed. This might explain the curve pattern after ultimate tensile stress, where small peaks are observed before rupture. The processes of nanopillar elongation, reconstruction, reordering, relaxation, and crystallization in a stepwise periodic manner before rupture produce a jerky curve pattern, while that of typical flexible plastic in bulk will show a smooth yielding curve.

The study indicates that the ultimate tensile stress for bulk PDMS ranges from 3.51 to 7.65 MPa. The ultimate tensile

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**Figure 4.** (A) Fabrication of mold with base dimension 98 nm, depth 43 nm and pitch 500 nm and (B) PDMS replica with base dimension 112 nm, height 70 nm and pitch 400 nm.
stress obtained from simulation also 46.3% of the bulk value, as summarized in Table 1. A study has revealed that elastic constant is less near the free surfaces compared to bulk values.\textsuperscript{39,40} For the nanostructure where the ratio of surface to volume is larger, the difference in mechanical strength of the nanostructure to its bulk value can be significant. Several factors contributed to this phenomenon, one of which is electron distribution. At the surface, electron distribution density is less, thus providing weaker bonding on the surface.\textsuperscript{41} Atoms further away from the surface experienced a different local environment compared to the atoms at the surface. However, for a nanostructure with a high surface to volume ratio, the electron distribution density is less throughout the structure. Furthermore, for a nanostructure with a characteristic length on the nanoscale, surface stress can displace atoms from their equilibrium positions, which are otherwise occupied in bulk assemblies. These changes in interatomic ordering can affect mechanical properties at the nanoscale.\textsuperscript{42} The Young's Modulus, Ultimate Tensile Stress, and Poisson's Ratio are summarized in Table 1.

In Figure 9, it is noted that Young's Modulus obtained from the simulation was 67–71% of the Young's Modulus values found in bulk PDMS of 1.32 MPa.\textsuperscript{35} One of the main factors that contributed to the reduction of simulated Young's Modulus in the experiment is the thermal effect at the
A study revealed that simulation conducted at low temperature i.e., $T = 50$ K has a larger Young’s Modulus than a simulation conducted at higher room temperatures of $T = 300$ K. This is because at higher temperature, atoms can absorb more energy, hence weakening the bonds between them and resulting in less stiff nanowire. At low temperatures of $T = 50$ K, the thermal effect is negligible. A high strain rate also can reduce stiffness by introducing disorder. However, for this study, the effect contributed by a high strain rate is minimized due to the low strain rate used, $\dot{e} = 0.01\% s^{-1}$. (Figures 10 and 11)

The Poisson’s ratio obtained from simulation is about 46.3% of the bulk value, which is less than the experimental bulk value of 0.4. When strain is applied and coupled with the thermal effect, the disorders within the nanostructure increase, hence increasing malleability and compressibility. An increase in malleability makes the PDMS nanostructure under uniaxial loading behave like a ductile structure, as indicated by Poisson’s ratio. Similar trends were found when stanene is subjected to uniaxial loading. A study by Koh et al. compares the changes in Poisson’s Ratio under the temperature effect, and the results show that Poisson’s Ratio at $T = 50$ K is significantly lower than Poisson’s Ratio at $T = 300$ K.

### CONCLUSIONS

The demolding process in soft lithography and nanoimprint lithography causes significant deformation on its replicated nanostructures. Experimental observations show clear signs of about 10–60% elongation on the replicated nanostructures after the demolding process. Hence, molecular dynamics simulations are employed to study the stress–strain relationship of the replicated PDMS nanostructures. The results from MD simulations demonstrate that the PDMS nanostructure at temperature $T = 300$ K under tensile stress shows characteristics of flexible plastic with significant yielding instead of the general pattern curve for bulk PDMS. Moreover, the PDMS nanostructure has a lower Young’s Modulus, which are around 67–71% of the bulk value. The Ultimate Tensile Stress for PDMS nanostructures is also about 46.3% of the bulk value and Poisson’s Ratio is about 48.0% as compared to the bulk value. This is due to the thermal effect, large surface to volume ratio, and characteristic length at the nanoscale. The results from this work have potential to be used as a guide for the nanofabrication/NIL process.

### MATERIALS AND METHODS

The mold used a positive electron beam resist polymethylmethacrylate (PMMA) of 150 nm thickness spin-coated on a silicon substrate at 4000 rpm for 60 s. After that,
the substrates were baked in an oven at a temperature of 185 °C for 30 min. The pattern was designed using Raith software and then exported to a Raith system in GDSII file format. Exposure of the nanosquare array was performed using a Raith ELPHY Quantum Plus EBL system integrated with a JOEL Scanning Electron Microscope (SEM) model JSM 6460LV at an acceleration voltage of 30 keV. The area dosage was fixed at 500 μC cm⁻², while the beam current was fixed at 0.02 nA. After EBL exposure, the exposed PMMA samples were developed in a mixture solution of methylisobuthyketone (MIBK) and isopropyl alcohol (IPA) with a proportion of 1:3 for 40 s, rinsed in IPA for 20 s, and dried by nitrogen gas. The pattern profile was then observed using an Atomic Force Microscope (AFM). The replication used the patterns defined in the PMMA resist without any further pattern transfer to minimize error. For the replica molding process, a PDMS prepolymer was degassed in a vacuum chamber and spin-coated at 1000 rpm for 40 s on a nanopatterned PMMA mold to produce a thin film of PDMS. The thin film of PDMS on the PMMA mold was degassed for the second time to assist the liquid mixture to fill into the cavities of the master mold before pouring the PDMS mixture until 2 mm of PDMS thickness was achieved. The PDMS mixture on the master mold was cured in the oven at 50 °C for 6 h. After the curing process, the crosslinked PDMS film was carefully peeled off from the PMMA mold. The pattern profile was then observed using an AFM.

The MD method used is a deterministic approach to calculate the dynamics trajectories of molecules, atoms, or ions. In general, the MD method can be divided into three stages. The first stage is to build the initial and boundary conditions. This includes the initial position, external forces, and interaction potential between particles. For this study, the monomers used are a series of PDMS chains of eight and 12. The packing and initial position were done using PACKMOL. The dimension of the PDMS substrate is 1000°, 1000°, and 1000 Å in the x, y, and z directions. The total number of atoms in the eight-series monomers is 1.21 × 10⁶ atoms, with 1 200 000 bonds, 2 268 000 angles, 28 008 000 dihedrals, and 1 440 000 improper interactions. For 12-series monomers, the total number of atoms is 1.45 × 10⁶ atoms, with 1 439 997 bonds, 2 723 991 angles, 3 383 991 dihedrals, and 1 727 991 improper interactions. In this stage, the substrate is minimized and equilibrated at temperature \( T = 300 \) K. In the second stage, the new positions and velocities of atoms were calculated and updated using the Newtonian equation of motion for every 0.01 fs. Large-scale Atomic/Molecular Massively Parallel Simulator, LAMMPS, is used as the main software to run the simulation. The simulation cell is deformed in the x-direction at a strain rate of 1.0¹¹ s⁻¹.
Author Contributions
This manuscript was written through contribution from all authors. All authors have given approval to the final version of this manuscript.

Notes
The authors declare no competing financial interest.

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