Molecular Simulation of Thermoplastic Polyurethanes under Large Compressive Deformation

Shuze Zhu(1), Nikolaos Lempesis(1), Pieter J. in ‘t Veld(2), Gregory. C. Rutledge(1)*

(1) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139.
(2) BASF SE, ROM/AM, Carl Bosch Str, 38, 67056 Ludwigshafen, Germany

*corresponding author. Email address: rutledge@mit.edu (G.C. Rutledge).

Abstract: Thermoplastic polyurethanes (TPUs) are candidates for a number of applications where outstanding resilience and ability to dissipate energy under large compressive deformation are needed. TPUs possess complex, heterogeneous structure where chemically distinct segments segregate into hard and soft domains, which pose significant challenges for the molecular level mechanistic understanding of their mechanical properties, and associated multi-scale modeling and experimentation. In this work, molecular simulations are used to identify the mechanism of mechanical response under large compressive deformation of a common thermoplastic polyurethane comprising 4,4′-diphenylmethane diisocyanate and n-butanediol (hard segment) and polytetramethylene oxide (soft segment), with atomistic resolution. The simulation employs a lamellar stack model constructed by the Interphase Monte Carlo method. This method creates an interfacial zone between hard and soft domains that satisfies both intermolecular packing and intramolecular connectivity constraints. Molecular-level mechanisms responsible for yielding, toughening, and the Mullins effect are reported. We have found several distinct mechanisms for yield and plastic flow in compression, which we categorize as (i) block slip, (ii) fragmentation and restacking, and (iii) block rotation.
The activity of these mechanisms depends on the topology of chains in the soft domain and the direction of loading (e.g. parallel or perpendicular to the interface). Further insights regarding the Mullins effect are garnered from cyclic loading at large compressive strains in this family of materials, where mechanisms (i) and (ii) were found to be major sources of energy dissipation, while the soft domain was found to be responsible for resilience. Together with our previous study on deformation mechanisms under large tensile strain, the current work expands our understanding of large strain deformation mechanisms for TPUs on the molecular level.
1. Introduction

Thermoplastic polyurethanes (TPUs) are linear, segmented multiphase, heterogeneous block copolymers. Their remarkable versatility, mechanical properties and chemical properties have made them suitable for a wide spectrum of applications.1-7 Outstanding toughness, durability and ease of processing are the most attractive features of TPUs for applications in high-performance structural materials, where the remarkable combination of elasticity and inelasticity is of vital significance. Therefore, the fundamental understanding of the mechanical properties of TPUs is important for the rational design and synthesis of advanced polymer-based structural and multifunctional materials with improved mechanical performance. Of particular importance are the molecular mechanisms responsible for mechanical resilience, the Mullins effect, and energy dissipation. The Mullins effect refers to a deformation-induced softening behavior observed during cyclic deformation, characterized by a lower stress upon reloading for the same applied strain. It is associated with significant mechanical degradation, energy dissipation, and hysteresis upon deformation. Nevertheless, molecular-level understanding has long remained elusive, despite a number of efforts using continuum mechanics modeling and experiments.8-10 They suffer either from the limitations of intrinsic modeling length scales, or from the resolution that can be probed experimentally.

Fortunately, state of the art computational molecular simulation offers a powerful approach to unveil fundamental molecular-level deformation mechanisms of a polymeric system. However, molecular simulations of TPUs are rarely reported in literature because their complicated heterogeneous morphology poses significant molecular modeling challenges. TPUs are copolymers composed of hard and soft segments, which segregate
on the nanometer length scale into hard and soft domains that are coupled mechanically through prolific interfacial zones that transmit stress through both intermolecular and intramolecular interactions. The hard domain is typically stiff and rigid, while the soft domain is typically compliant and flexible. Relatively ordered aggregates of the hard segments are interspersed at random orientations within an amorphous polymer matrix composed of soft segments. To tackle the molecular modeling challenges towards obtaining fundamental insights, we recently reported a first-of-its-kind molecular modeling effort focused on TPU s under deformation to large tensile strains, using atomistic Monte Carlo and molecular dynamics simulations. \(^1^1\) We constructed a detailed, thermodynamically rigorous, atomistic model of the interfacial zone between hard and soft domains within TPU s, with thermodynamically consistent distributions of soft segments that connect hard domains through bridges, loops and tails. We examined how the topology of loop and bridge segments within the soft domain affects the mechanism of large tensile deformation for a common type of TPU, in which the hard segment is 4,4’-diphenylmethane diisocyanate (MDI) with n-butandiol (BDO) as chain extender\(^1^2\) (henceforth denoted as MDI/BDO) and the soft segment is poly(tetramethylene oxide) (PTMO). \(^1^3\) Under large tensile deformation, we found several distinct mechanisms for plastic deformation, which we categorized as (i) cavitation, (ii) chain pull-out, (iii) localized melting with shear band formation, and (iv) block slip. Those mechanisms depend on the topology of segments in the soft domain and the direction of loading (e.g. parallel or perpendicular to the interface). From cyclic loading, we found that mechanisms (ii) to (iv) are the dominant toughening mechanisms, and are responsible for
the Mullins effect, superior resilience and dissipation of energy at large tensile strains in TPU

Nevertheless, the subsequent investigation of the deformation mechanism of TPU s under large compressive strains suggests a few distinct mechanisms in addition to those observed under large tensile deformation. In the current work, we report our observations of compressive deformation in TPU s, with particular focus on those distinct mechanisms; where mechanisms observed are similar to those in tension, our discussion is brief. In particular, the block slip mechanism found at large tensile strains is also observed at large compressive strains, but is not discussed in detail. We also discuss the source of resilience in TPU s during cyclic loading, which was not discussed in the study of large tensile deformation. To our knowledge, this is the first such model of the large compressive deformation mechanisms of a TPU, with atomistic resolution. Along with our previous study on large tensile deformation of TPU s, the current work augments our molecular-level description of deformation mechanisms of TPU s at large strain. It is our hope that this work may facilitate future development of multi-scale theoretical and experimental approaches to engineer the multiphase heterogeneous polymers with complex structure but vitally important mechanical properties.

2. System and Methods

For this study of TPU response in compression, we use the same systems and methods as described in our previous report of TPU response in extension, where a more detailed explanation on model construction can be found. For the sake of completeness, the details
of models construction are briefly recapped below, but the reader is referred to the previous report\textsuperscript{11} for a more complete description. We use the Interphase Monte Carlo (IMC) method of Rutledge and co-workers\textsuperscript{13-19} as implemented in the EMC (Enhanced Monte Carlo)\textsuperscript{16} software (version 9.3.7) to construct the model. The force fields were previously validated on simulations of semicrystalline PTMO,\textsuperscript{13} and crystalline MDI/BDO.\textsuperscript{12} Atomistic configurations of TPU's were created using the IMC method, having a crystalline MDI/BDO layer and an amorphous PTMO layer. In general, the model created by the IMC method is a one-dimensional lamellar stack that consists of noncrystalline domains sandwiched between crystalline domains, as shown in Figure 1. The sizes of the hard and soft domains in the x-direction were based on X-ray diffraction data, which indicates a typical hard domain thickness of four MDI/BDO repeat units\textsuperscript{20-25}, and compositional information, which dictates the volume fractions of hard and soft domains (or their thicknesses). The mass fraction of hard domain in the TPU of this study was roughly \(55 \pm 2\%\), for which experimental characterization has been reported previously.\textsuperscript{9} The topology of the interphase is characterized by the set of loops, bridges, and tails within the PTMO soft domain. “Bridges” span the soft domain and connect two hard domains through an intra-molecular linkage, “loops” connect two points in the same hard domain, and “tails” terminate somewhere in the soft domain. The Interphase Monte Carlo (IMC) method uses a combination of local and global Monte Carlo moves to equilibrate the system with respect to topological degrees of freedom. Both hard and soft domain layers are semi-infinite due to periodic boundary conditions in the lateral directions, and the lamellar stack repeats due to periodic boundary conditions in the stack direction. Chain connectivity between hard and soft segments was maintained throughout
the simulation. Hydrogen bonding between hard segments is represented implicitly through a combination of Coulombic and Lennard-Jones interactions. In our previous study, we showed that the hydrogen bonds have realistic energies of about 14.98 kJ/mol, and are oriented within planes that are nearly parallel to the y-direction of the hard domain (Figure 1(b) and Figure S1). For the ease of discussion hereinafter, we equate the y-direction with hydrogen bonding plane orientation. The PTMO segments within the soft domain are colored-coded throughout this report (cf. Fig 1 caption for details) unless otherwise specified.

As starting configurations for compressive deformation, we use the same 15 TPU configurations that were previously used for tensile deformation (i.e., “configuration #1” has the same meaning in both works). They were generated by unbiased sampling from the equilibrium distribution of topologies created by the IMC method. Categorization of these configurations according to topological ensemble (either “no bridges” or “with bridges”) can be found in Table 1. Configurations categorized as “With bridges” have at least one bridge segment or bridging entanglement between loops emanating from opposite interfaces; configurations categorized as “No bridges” have neither of these topological entities.

| System topological category | Configuration # | # of bridges | # of loops | # of loop-loop bridging entanglements | # of tails |
|----------------------------|----------------|--------------|------------|-------------------------------------|------------|
| No bridges                 | 1              | 0            | 75         | 0                                   | 50         |

Table 1. Configurations of TPUs Studied in This Work
| No bridges | 2 | 0 | 25 | 0 | 150 |
|------------|---|---|----|---|-----|
| No bridges | 3 | 0 | 5  | 0 | 190 |
| No bridges | 4 | 0 | 43 | 0 | 114 |
| No bridges | 5 | 0 | 37 | 0 | 126 |
| With bridges | 6 | 8 | 52 | 0 | 80  |
| With bridges | 7 | 15 | 48 | 0 | 74  |
| With bridges | 8 | 6 | 39 | 0 | 110 |
| With bridges | 9 | 10 | 24 | 0 | 132 |
| With bridges | 10 | 0 | 59 | 1 | 82  |
| With bridges | 11 | 0 | 45 | 1 | 110 |
| With bridges | 12 | 0 | 44 | 2 | 112 |
| With bridges | 13 | 5 | 58 | 1 | 74  |
| With bridges | 14 | 14 | 47 | 2 | 78  |
| With bridges | 15 | 10 | 58 | 2 | 64  |

As before, these configurations were imported to LAMMPS\textsuperscript{26} for subsequent molecular dynamics simulation. All configurations were first equilibrated by molecular dynamics simulations in the $N\sigma T$ (N denotes total number of UA sites, $\sigma$ is stress, and T is temperature) statistical ensemble at $T=300$ K and $P=1$ atm, using the Nosé–Hoover thermostat and barostat (temperature damping parameter was 50 time steps and stress
damping parameter was 500 time steps), respectively. The time step was 2 fs. All normal stress components were equal to about 1 atm, all shear stress components were close to zero, and the density of the system was converged.

After equilibration, compressive deformation was applied using nonequilibrium molecular dynamics simulation in which one dimension of the simulation box was decremented at each step of the simulation, to produce constant strain rate deformation in an \( \text{N} \sigma_{ij} \varepsilon_k \text{T} \) ensemble, up to a maximum engineering compressive strain of 50%. Three orthogonal loading directions (x, y and z) were considered. The lamellar stack was deformed in one of the three principal directions (henceforth called the “loading direction”) at a constant engineering strain rate, while maintaining a constant (negligible) stress (1 atm) along the other two directions. Thus the dimensions orthogonal to the loading directions were free to change in response to Poisson’s effect. The temperature was maintained at 300 K. The time step was 2 fs, and the engineering strain rate was \( 5 \times 10^7 \text{ s}^{-1} \). After equilibration, the simulation box sizes of the 15 configurations were typically about 28 nm along the stack direction and 5 nm along the lateral directions (Fig. S1). The simulation sizes were mainly dictated by a compromise between atomistic resolution and computational cost. The instantaneous stress tensor components of the system were computed according to the method proposed by Irving and Kirkwood.\(^{27}\) Time averages of the six stress tensor components were taken at frequent time intervals during the entire simulation. Engineering stress-strain curves are reported. The stress component along the loading direction is reported as stress. For cyclic loading, the unloading stopped when the stress was at or about to cross zero. All simulations were re-
equilibrated using molecular dynamics simulations in the NoT statistical ensemble at T=300 K and P=1 atm between the first unloading and the second loading.

Figure 1 (a) Schematic showing the TPU system, containing crystalline hard domains and amorphous soft domain, which was constructed by Interphase Monte Carlo moves. The soft domain contains soft polymer chains characterized as topological features including “tail”, “loop” and “bridge”. The polymer chains within the soft domain are colored according to segment topological type: tails (green), loops (red), and bridges (blue). This color code is used consistently throughout this report unless otherwise specified. The hard domain, contains hydrogen-bonded hard segments. We used the same set of TPU systems from our previous report of large tensile deformation mechanisms, where more details about model construction are given. (b) Schematic showing the formation of a hydrogen bonding plane in the hard domain. It is critical to note that in the models of current study, hydrogen bonds between segments in the hard domain occur within planes that are nearly parallel to the y direction. Note that the orientation of the coordinate axes in (b) is the same as in (a).

3. Results and Discussion

3.1 Stress-Strain Behavior in Compression to Large Deformation

Figure 2 shows the stress-strain curves in x, y, and z directions for compressive deformation of the simulation cell. Results are shown for the “No bridges” and “With bridges” sub-ensembles (configurations 1-5 and 6-16, respectively), as well as for the
total ensemble of all 15 configurations. The stress-strain curves are averaged over trajectories initiated at every configuration in the ensemble. The responses in compression are quite different from those observed in tension, reported previously. For compression along the x direction, the mechanical response is qualitatively similar for all three ensembles, indicating that the large deformation behavior might be insensitive to topology. In Figure 2(a), the stress-strain curve for the total ensemble exhibits a few noticeable yield events. For example, the first yield occurs around a strain of 20%, with a yield stress around 130 MPa, and the second yield occurs around a strain of 33%, with a yield stress around 80 MPa. By contrast, compressive deformations along the y- and z-directions are sensitive to topology. In the y-direction, the “No bridges” sub-ensemble in Figure 2(b) exhibits a single noticeable yield event, at about 4% strain with a yield stress around 50 MPa, while the stress in the “With bridges” sub-ensemble rises gradually to a much higher yield stress (200 MPa) at much larger strain (30%). Close examination of this stress-strain curve reveals tiny sawtooth features (shown in inset) after such yield event. In the z-direction, the response is qualitatively similar to the y-direction, albeit with somewhat lower maximum stresses. For loading along both y- and z-directions, the magnitude of stresses in the stress-strain curves of the “No bridges” sub-ensemble are similarly small, and they both yield at relatively small strain; in addition, the shapes of the stress-strain curves of the “With bridges” sub-ensemble look similar, in the sense that they all experience a nearly linear increase in stress over a wide strain range until the yield event occurs at a large strain (near 30%), even though they are quantitatively different. Therefore, there could be a qualitatively similar compressive deformation mechanism for loading along y- and z-directions. Nevertheless, the stress-strain curves
for loading along the x-direction are qualitatively different from those along the y- and z-directions.

Figure 2. Engineering stress-strain curves (the stress reported here is the stress component along the loading direction) in compressive deformation, averaged over “No bridges” configurations only (first row), “With bridges” configurations only (second row), and all configurations (third row). Columns separated by dashed lines denote corresponding loading directions (x, y and z), which are orthogonal to each other. Purple arrows on stress-strain curves point to salient yield events. All compressive strains are reported as absolute values. Refer to Section 3.1 for a summary of these mechanical responses and Section 3.2 for detailed mechanisms to account for these responses.

3.2 Molecular Interpretation of Stress-Strain Response in Compressive Deformation

Our goal here is to gain molecular insights that can explain the mechanical properties of TPUs under large compressive deformation. This can be achieved from molecular simulation, which allows one to inspect the molecular rearrangements that accompany
deformation, with atomistic resolution. Specifically, we can understand the stress-strain curves in Figure 2 by identifying the structural evolution of hard and soft domains during compression for each configuration in the ensemble. In this work, we focus more on the mechanisms that are distinct from those of tensile deformation, while keeping brief the discussion of mechanisms similar to those observed in tensile deformation.

Referring back to Figure 2, we formulate our discussion here around four questions that arise upon examination of the TPU response to compressive deformation. Question #1: Why does the mechanical response in the x-direction look so different from those in y- and z-directions? Question #2: Why does the mechanical response of the “With bridges” sub-ensemble in the y-direction have the highest yield stress among all combinations of compression direction and topological sub-ensemble? Question #3: Why does the “No bridges” sub-ensemble exhibit a clear yield event when strained in the y-direction, but undergoes plastic flow readily when strained along the z-direction? Question #4: Why does the “With bridges” sub-ensemble exhibit small sawtooth features in the stress-strain curve after yield? To address these questions, we illustrate with a set of representative configurations that can best highlight the associated mechanism. In fact, we have inspected the structural evolutions of all configurations within an ensemble and confirmed that the highlighted behavior holds universally.
Figure 3. The engineering stress-strain curves (the stress reported here is the stress component along the loading direction) and structural evolution of configuration #1 (from the “No bridges” sub-ensemble) (a) and configuration #7 (from the “With bridges” sub-ensemble) (b) during compressive straining along the x-direction. The mechanical perspective of shear stress is depicted in (c). The blue arrows in (a) serve as a guide to the eye, indicating the rotation of hard domain orientation. The block slip happens when blue arrow #2 is about 45 degrees to the x-direction. Only bridges in the soft domain are colored blue in (c) for highlight. The block slip mechanism is identified for both sub-ensembles.

To address Question #1, Figure 3 shows the deformation mechanism of the lamellar stack under compressive deformation along the x-direction. Two configurations are presented, one from each topological sub-ensemble. The stress-strain curves look similar in terms of the features of stress decrease at large strain. In the range of strain from 0% to 15%, compressive deformation along the x-direction compacts the lamellar stack as though the soft and hard domains were resistances in series; most of the strain is therefore carried by the soft domain. We find that in such strain range (from 0% to 15% strain), the entire
hard domain rotates (a more detailed illustration is provided in Figure S2), which can be regarded as its mechanical response to the lateral pressure exerted by the soft domain at the interface. Later, block slip occurs at the yielding point. The block slip behavior in the hard domain is caused by shear stress (Figure 3(c)), and has been also observed in large tensile deformation. Such a similarity can be readily understood by the Poisson effect: the lamellar stack under serial compression is qualitatively similar to that under lateral tension. As a result, some of the tensile deformation mechanisms may apply. For the block slip to happen, the compression-induced shear stress has to exceed the interfacial strength between planes of hard segments. From continuum mechanics, we expect the critical resolved shear stress to peak at an angle of 45 degrees to the loading direction. As the rotation continues and the in-plane direction of planes of hard segment (e.g., the #2 blue arrow in Figure 3(a)) approaches 45 degrees to the compression direction, the shear stress between planes of hard segments reaches its maximum. At this configuration, the rotation is expected to stop, and the shear stress builds until block slip occurs. For the 15 configurations in this study, we found that the strain at which the first yield event occurs is distributed almost randomly between 15% to 25% strain, but that block slip generally occurs when the slip plane approaches the 45 degree orientation. The number of such yield events appearing in the stress-strain curves varies from configuration to configuration. As a result, the stress drops appear to be “rounded off” when ensemble averaged, as is the case in Figure 2(a).
Figure 4. The engineering stress-strain curve (the stress reported here is the stress component along the loading direction) of configuration #2 (from the “No bridges” sub-ensemble) during compressive deformation along the y direction (a), and along the z direction (b). (c) Structural evolution of the hard domain of configuration #2 during compressive deformation along the y direction. Carbon atoms (yellow) are highlighted. The two structures are shown with the scale. The structural evolution indicates rotation, and is not to be confused with fine slip, as the distance between the layers of hexagonal carbon rings (labeled as L) does not reduce drastically during deformation (see the right panel). The purple and blue surface points are guides to the eye for the visualization of rotation. Keep in mind that the simulation cell is periodic. (d), (e), and (f) show the typical structural evolution of a slice from the hard domain containing two layers of hard segments. The red parallelogram indicates the relative positions of four aromatic ring groups. As the structure rotates, shown by the changing orientation of the coordinate axes, such red parallelogram configuration remains essentially undeformed, confirming that the hard domain is merely undergoing a rotation. The inset in (f) shows the view through multiple aromatic rings in one layer of hard segments. Such a view is generally preserved during rotation, suggesting a largely undisturbed crystalline structure in the hard domain during rotation.

To answer Questions #1 and #3, Figure 4 shows the deformation mechanism of the lamellar stack under compressive deformation along the y- and z-directions for configuration #2 (“No bridges”). One can see that the stress-strain curves look qualitatively similar. They both show plateaus in stress after the yield event, indicative of plastic flow. However, the stress-strain curve in Figure 4(a) has a yield strain around 3%,
while the stress-strain curve in Figure 4(b) exhibits a much weaker stress roll-over at small strain. It turns out that the pre-yielding range in the stress-strain curve in Figure 4(a) is due to the compression of the hard domain, while yield and the subsequent plastic flow for both loading directions are accompanied by rotation of the hard domain (e.g., the rotation of the pair of purple and dark blue points in Figure 4(c); a more detailed illustration is presented in Figure S3), which does not further increase the stress level. The plastic flow stress is then mainly caused by the viscoelastic deformation within the soft domain. The yield event correlates well with the onset of rotation of the hard domain (see Figure S4 and Figure S5). To convince that the hard domain rotates as a rigid body rather than undergoing slip, Figure 4(d)–(f) illustrate the rotation of a slice in the hard domain containing two layers of hard segments, as the compression occurs along the y direction. The red parallelogram marks the relative positions of four aromatic rings; it remains largely intact during compression, but rotates as confirmed by the rotation of the coordinate axes. The inset in Figure 4(f) shows the view through multiple aromatic rings in one layer of hard segments. Such a view is generally preserved, indicating that the crystalline structure in the hard domain is largely unperturbed during rotation.

To understand why compression along the y-direction gives rise to a linear increase in stress before yield, while compression along the z-direction gives rise almost immediately to plastic flow, one has to refer back to the orientation of hydrogen bonding planes (Figures 1(b)). Compression along the y-direction deforms the hydrogen bonds within a plane, while compression along the z-direction does not (Figures S1). Since the previous analysis of hydrogen bonding energy\(^\text{11}\) has shown that the depth of the energy well for compression in-plane (e.g., along the y-direction) is deeper than that for
compression out-of-plane (e.g., along the z-direction), the y-direction can accommodate more compressive strain; this behavior appears as the pre-yielding range in the stress-strain curve. On the other hand, compression along the z-direction does not have such a buffering mechanism; therefore, rotation is soon observed in the hard domain, which induces stress flow to mitigate the stress increase.

**Figure 5.** The engineering stress-strain curve (the stress reported here is the stress component along the loading direction) of (a) configuration #9 (from the “With bridges” sub-ensemble) during compressive straining along the y-direction and (b) The engineering stress-strain curve of configuration #9 during compressive straining along the z-direction. (c) Structure evolution of configuration #9 during compressive straining along the y-direction. Only bridges in the soft domain are colored blue. The curvy feature of straightened bridges also indicates rotation of hard domain. (d), (e), (f), (g) show the structural evolution of a slice in the hard domain containing two layers of hard segments. The rotation can be inferred from the rotation of coordinate axes. The inset in (d) shows a view through multiple aromatic rings in one layer of hard segments. Such a
view (on the same arrays of aromatic rings) is tracked during rotation as these insets in (e), (f) and (g), and suggests a disordered restacking process in the hard domain. (h) Schematic use to illustrate “restacking” to accommodate the compression.

To answer Questions #2 and #4, Figure 5 shows the deformation mechanism of the lamellar stack under compressive straining along y- and z-directions for configuration #9 (“With bridges”). It turns out that the high stress level of the “With bridges” configuration originates from the stretching of bridges during the rotation, as shown in Figure 5(c). This stretching of bridges arises due to shear of the soft domain required to accommodate rigid body rotation of the hard domains. The stress increases almost linearly until the first significant stress drop around 30% strain. Here we define such significant stress drop as yield. The mechanism of yield is illustrated in Figure 5(d)–(g). As rotation continues, the strain energy in the soft domain accumulates due to the stretching of bridges, and the energy barrier for the hard domain to rotate as a rigid body increases. At some point, rotation is no longer an energetically favorable process to mitigate the incremental increase in strain energy at an infinitesimal compressive straining step. At this point, yield occurs through restacking of the hard domain, which releases strain energy and manifests as a drop in stress, and therefore accommodates the compressive deformation. Here, “restacking” refers to the lateral displacement of hard segments within the hard domain to accommodate the compressive strain (Figure 5(h)). (Figure S6 and Figure S7). Figure 5(d)–(g) illustrate the transition between the rotation of a slice in the hard domain containing two layers of hard segments and its restacking, as compression proceeds along the y-direction. The rotation can be inferred from the change of orientation of coordinate axes. As the bridges become increasingly stretched, the rotation eventually stops. With increasing compressive deformation, the hard segments
have no other way but to change their molecular stacking pattern to accommodate the compression, and therefore the restacking is set into motion (Figure 5(h)). The inset in Figure 5(d) shows a view through multiple aromatic rings in one layer of hard segments. Such a view on the same arrays of aromatic rings is tracked during rotation as these insets in Figure 5(e), 5(f) and 5(g), and suggests a restacked structure in hard domain. It is also important to note that, in addition to the hydrogen bonding, the stacking interactions between aromatic rings are important to the stability of hard domain.\textsuperscript{11}

\textbf{Figure 6.} Fragmentation of hard domain into smaller domains during the restacking process. The compression is applied along the \textit{y}-direction. Fragmentation can be identified by the
misalignment of hydrogen bonding planes in hard domain of configuration #9 (sub-ensemble: With bridges). Strain values are labeled, and indicated on the stress-strain curve by arrows (same as Figure 5(a)). Two grains with misaligned hydrogen bonding planes are shown. Here two sets of viewing perspectives (left column and right column, inferred by the change of visibility of top/bottom face of the simulation cell, and the rotation of the coordinate axes; for example, the viewing direction difference is about 7 degrees at strain 31%) are provided for better visualization. Individual grains are distinguished by the types of circles used to highlight them. The fragmentation gives rise to the salient drop in stress (see the arrows), and stress accumulation (increase in stress) is needed for the next fragmentation to occur.

For the “With Bridges” sub-ensemble, salient sawtooth features are observed in the stress-strain curve for compressive straining along the y-direction (Figure 5(a)), while there are almost no such features for the z-direction (Figure 5(b)). We further notice that the compressive strength along the y-direction is significantly higher than that along the z-direction. This is in agreement with Figure 2. For compressive deformation along the y-direction, we find that restacking first transforms the crystalline hard domain, which initially has a uniform orientation of hydrogen bonding planes, into multiple crystalline grains characterized by different orientations of the hydrogen bonding planes (Figure 6). Such crystalline grains evolve as the compression strain increases. The initial hard domain can be regarded as a single crystalline grain. At 31% compressive strain, the fragmentation of this single grain into smaller grains is observed, accompanied by a considerable decrease in stress. Here, fragmentation involves a rearrangement of intermolecular interactions only; no covalent bond breaking was allowed. Further fragmentation requires additional external work, which increases the stress level until the next fragmentation event is initiated, at which point the stress drops again. Such repeated processes give rise to the sawtooth features. The increasing fragmentation of the hard domain into smaller and smaller grains results in the final disordered stacking pattern of hard segments, and not even small crystalline grains can be found. Monitoring the
evolution of the number of hydrogen bonds during deformation indicates that there is a gradual reduction in the number of hydrogen bonds before the onset of fragmentation (Fig. S8). After fragmentation, the number of hydrogen bonds is restored, in a kind of “self-healing”. Such breaking and reforming of hydrogen bonds is expected to dissipate a lot of energy. Such a mechanism is much more frequently observed for compression along the y-direction, which explains its more pronounced sawtooth structure in the ensemble averaged stress-strain curve (Figure 2). For compression along the z-direction, it is not typical to observe such well-identified repeated fragmentation events during the restacking of the hard domain (Figure S7). We believe that such sharp contrast in structural evolution for the two orthogonal lateral directions could be traced to orientation of the hydrogen bonding planes, which are nearly parallel to the y-direction. Apparently, more energy is dissipated from the breaking and reforming of hydrogen bonds with compression within the plane of the hydrogen bonds of the hard domain (i.e. y-direction) than with compression between planes of hydrogen bonds of the hard domain (i.e. z-direction); this conclusion is based on the comparison between the maximum stresses and the areas beneath the stress-strain curves (e.g., compare those in Figure 5(a) and 5(b)), which indicates the mechanical work performed on a highly disordered hard domain. Thus it also suggests that the orientation of hydrogen bonding planes is critical for achieving a high compressive strength, which will be evidenced later from cyclic loading.

3.5 Resilience and Energy Dissipation from Cyclic Compressive Deformation

Given our understanding of deformation mechanisms under large tensile strain, and the mechanisms discussed above for large compressive strain, we offer next a mechanistic
interpretation of the stress-strain curves of the lamellar stack under cyclic compression, particularly for the molecular origins of recovery, toughening and the Mullins effect. Here, we only consider cyclic deformation in the x- and y-directions; the response in the z-direction is quantitatively similar to that in the y-direction, and has a similar interpretation. We find that the block slip mechanism associated previously with the Mullins effect in tension\(^{11}\) applies as well in compression. We emphasize here the new findings that are observed exclusively for compression deformation, while only briefly mentioning the similar mechanism with the tension deformation.

![Stress-strain curves](image)

**Figure 7.** Stress-strain curves (the stress reported here is the stress component along the loading direction) during cyclic compression loading. Note the stress scales are different. The first loading curve is shown in blue; the unloading curve is shown in green and the second loading curve is shown in purple. Configuration #1 (from the “No bridges” sub-ensemble): (a) first compressive loading along the x-direction; (b) and (c) unloading from 20% and 40% strain, respectively, in the first loading, followed by reloading along the x-direction. Configuration #2 (from the “No bridges” sub-ensemble): (d) first compressive loading along the y-direction; (e) and (f) unloading from 20% and 40% strain, respectively in the first loading, followed by reloading along the y-direction. Configuration #9 (from the “With bridges” sub-ensemble): (g) first compressive loading along the y-direction; (h) and (i) unloading from 20% and 40% strain, respectively, in the first loading, followed by reloading along the y-direction. Superior resilience
and energy dissipation of TPU under compression are demonstrated from these stress-strain curves during cyclic loading.

Figure 7(a) shows the stress-strain curve for loading a typical configuration from the “No bridges” sub-ensemble in the x-, or lamellar stack, direction. Figure 7(b) shows the same system after unloading from 20% strain, a point in the first loading cycle that precedes the first yield event. The unloading and reloading curves retrace the initial loading curve almost exactly, indicating that the resilience of this TPU within this compression range is significant. Since the soft domain sustains most of the normal compressive stress along this loading direction, we can conclude that the soft domain is the main source of resilience of TPU under compression. In contrast to Figure 7(b), Figure 7(c) shows the same system after unloading from 40% strain, a point in the first loading cycle that follows several yield events, and reloading. In this case, the stress-strain curves are not retraced below the unloading point; the deformation is not fully recoverable. Beyond the unloading point, the curves are retraced. This behavior is evidence of plastic deformation and can be traced to the onset of block slip in the hard domain, which is not recoverable. The onset of plasticity by the mechanism of block slip accords with similar observations during tensile deformation of TPUs.\textsuperscript{11} This stress-strain curve demonstrates the strong Mullins effect, where a huge amount of energy is dissipated.

Figure 7(d) shows the stress-strain curve for compression of a typical configuration from the “No bridges” sub-ensemble in the y-, or lateral, direction. Figure 7(e) and 7(f) then show stress-strain curves for unloading and reloading of this system from initial compressive strains of 20% and 40%, respectively. These two curves look qualitatively similar. In both cases, the strain recovered is about 15%, and is not large enough to
restore its original state. This is the consequence of non-recoverable, energy-dissipating viscoelastic deformation (e.g., sliding between chains under shear stress) within the soft domain during compression. The stress-strain curve of the second loading is characterized by lower stress than that of the first loading at the same strain, up to the unloading point. Beyond the unloading point, the stress-strain curve for second loading roughly traces that for the first loading. The softer mechanical response can be directly related to the changed orientation of the hard domain. Our initial model allows for a certain degree of compression of the hard domain before it rotates; it is such initial compression that offers an immediate linear increase in the stress. Then, the rotation of hard domain and viscoelastic deformation within the soft domain give rise to a state of plastic flow. Therefore, since the orientation of hard domain cannot fully recover to the initial state upon unloading due to the viscoelastic deformation within the soft domain, the hard domain cannot have the same level of mechanical response and should slowly reach the flow stress state by further rotating until it picks up the configuration around which the unloading starts.

Figure 7(h) shows the stress-strain curve for the unloading and reloading of a typical configuration from the “With bridges” sub-ensemble in the z-, or lateral, direction, starting from a point of 20% strain in the first loading (Figure 7(b)), prior to yield. Note that bridges are involved. The unloading and reloading curves retrace the stress-strain behavior observed in the first loading curve (Figure 7(g)), with the exception that there is a bit of softening at the initial stage of unloading. This linear response indicates the relaxation of straightened bridges (Figure S9). This also reveals another source of the TPU’s superior resilience under compression, in addition to the compression of the soft
domain under normal stress (discussed in Figure 7(b)). Similar to the understanding associated with Figure 7(e), the hysteresis in the stress-strain curve during first loading and unloading in Figure 7(h) is a consequence of non-recoverable viscoelastic deformation within the soft domain (e.g., sliding among soft chains). The ensuing stress-strain curve from second loading is only slightly below the first loading curve up to strain 12%, exhibiting only a very slightly softer mechanical response. Further loading gives an almost overlapped linear mechanical response, which is understandable since the dominating deformation mechanism is now again the straightening of bridges. A different sawtooth shape is observed in second loading, but the first few strains at which the stress sharply drops remain similar to that of first loading. This sawtooth shape also suggests the repeated, non-recoverable fragmentation of hard domain into smaller grains (e.g., Figure 6).

Figure 7(i) shows the stress-strain curve for the cyclic loading/unloading from 40% strain, which exceeds the yield strain in first loading. Similar to the unloading from 20% strain, the major portion of the unloading curve parallels the linear part of first loading curve, which involves the relaxation of bridges. Energy dissipation can be interpreted from the area enclosed by the stress-strain curves during first and second loading. Unlike unloading before restacking happens, the major portion of energy dissipated is from the restacking (e.g. repeated fragmentation) in the hard domain, which is irreversible (Figure S9). Furthermore, the ensuing stress-strain curve from second loading exhibits a significantly softer mechanical response (about 150 MPa less in stress), compared with the stress value from first loading at same strain. Beyond the unloading point, the stress-strain curve from second loading picks up that from first loading. These observations are
typical of the Mullins effect. The understanding is that the fragmented hard domain is not able to recover to its initial state upon unloading. Therefore, in second loading, the hard domain does not need to repeat the destruction of its crystallinity and responds with a significantly less stress. Combined with the block slip discussed earlier, we can see that the non-recoverable deformation in the hard domain is the dominating energy dissipation mechanism under compression, in accordance with the tensile case.\textsuperscript{11}

4. Concluding Remarks

In this study, we report the molecular mechanisms operative during large compressive deformation of a common type of thermoplastic polyurethane, using molecular dynamics simulations. Deformations were performed at constant strain rate, up to engineering strains of 50\% in compression. The TPU model was constructed using the Interphase Monte Carlo (IMC) method, previously developed for semicrystalline polymers. We use the same models and similar approaches to those employed in our previous study of the tensile deformation mechanisms.\textsuperscript{11} The large deformation mechanisms are presented in the context of two topological sub-ensembles, three orthogonal loading directions (x, y, and z), and cyclic loading.

A rich variety of molecular scale mechanisms is revealed within these TPUs through a detailed examination of the structural changes during compression and cyclic loading, some of which are recoverable and others that are not. In compression, the non-recoverable changes, responsible for the energy dissipation, mainly involve destruction of the hard domain, in the forms of block slip, block rotation of the hard domain,
fragmentation and disordered restacking in the hard domain. The recoverable changes, responsible for resilience, mainly involve deformation in the soft domains. Both compression of the soft domain due to stress in the stack direction, and stretching of the bridging segments during compression-induced shear deformation in soft domain contribute to the resilience.

Since hydrogen bonding is important for the hard domain to maintain the crystal phase, it is expected that fragmentation and disordered restacking are related to the breaking and reforming of hydrogen bonds. The rigid body rotation of the hard domain is typically the precursor to these destructive events. The release of hydrogen bonding energy is the physical source of energy dissipation. The block slip mechanism, already observed in large strain tensile deformation, still dissipates a considerable amount of energy, although it does not usually require breaking of hydrogen bonds. We conclude that the irreversible deformation of the hard domain is the major source of the Mullins effect. The energy dissipated within the soft domain by its viscoelastic behavior is typically much less than that from the hard domain.

Combined with our previous studies of small strain deformation and large tensile deformation of TPUs, the current work expands our study of the molecular level deformation mechanism of TPUs using molecular simulation. The relative importance of the mechanisms observed may vary with strain rate, but are subject to activation at any strain rate. It is possible that additional mechanisms not observed in this work may be activated at slower strain rates, but those are beyond the reach of current molecular dynamics simulations. An accurate description of the experimentally measurable
mechanical response of a TPU would require, at a minimum, a multi-scale model that includes a distribution of lamellar stacks in various orientations. Consideration of the lamellar stack comprising layers of greater lateral extent could give rise to something like plate buckling instabilities\textsuperscript{30} under certain conditions, but such instabilities were not observed here. The mechanisms observed in this work could be potentially important in shock deformation as well.\textsuperscript{31, 32} For example, the block slippage and fragmentation mechanisms in the hard domains, and the viscoelasticity of the soft domains, could serve to dissipate the energy of a pressure or shock wave. We believe that the effect of the block slippage and fragmentation mechanisms should be included in any theoretical description of the mechanics of such TPU\texttext{s. Ultimately, we envision that the molecular mechanisms extracted from these simulations can be used to inform future multi-scale theoretical and experimental approaches to engineer the multiphase heterogeneous polymers with complex but vitally important mechanical properties.}

5. Supporting Information

Simulation box, hydrogen bonding plane configuration, supplementary structure evolution data, variation of number of hydrogen bonds during loading.

6. Acknowledgement

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