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Sliding wear behavior of polymers studied with mesoscopic molecular dynamics

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ABSTRACT

Insufficient attention to tribology of materials, including friction, scratchability, and wear, causes severe financial losses in industry. Despite this situation persisting for decades, scratch resistance is still not sufficiently understood. This applies even more to sliding wear, which is multiple scratching along the same groove. We have employed molecular dynamics computer simulations to study sliding wear of amorphous polymeric materials. Our simulations pertain to a coarse-grain model of high-density polyethylene. The obtained results include analysis of penetration depth, residual depth, segment displacement as a function of time, and recovery percentage for a range of indenter diameters and force magnitudes. Effects of each of these parameters on the tribological properties are evaluated, providing useful information that can enable tailoring materials for specific applications.

Introduction

As argued eloquently and in detail by Rabinowicz in his book, the tribological properties of materials are important for their service performance, and thus also for the economic performance of the industry [1]. Tribology is the study of friction, scratchability, and wear—and also of methods to mitigate these effects such as by lubrication [1–6]. Scratch testing also provides a measure of adhesion of a coating to a substrate [7, 8].

Wear occurs when two materials come into contact and slide against one another. While wear of metals can be mitigated by lubrication, the same method cannot be applied to polymer-based materials (PBMs) since a liquid lubricant will likely be absorbed by the polymer, causing swelling. PBMs are often used in applications that are susceptible to wear such as surface coatings or in polymer-based composites. Therefore, owing to unmitigated wear, otherwise mechanically sound moving parts have to be replaced by new ones—which in some cases can be an expensive and unsustainable long-term strategy. Moreover, scratch resistance is important also because a scratch can become the origin of crack propagation.

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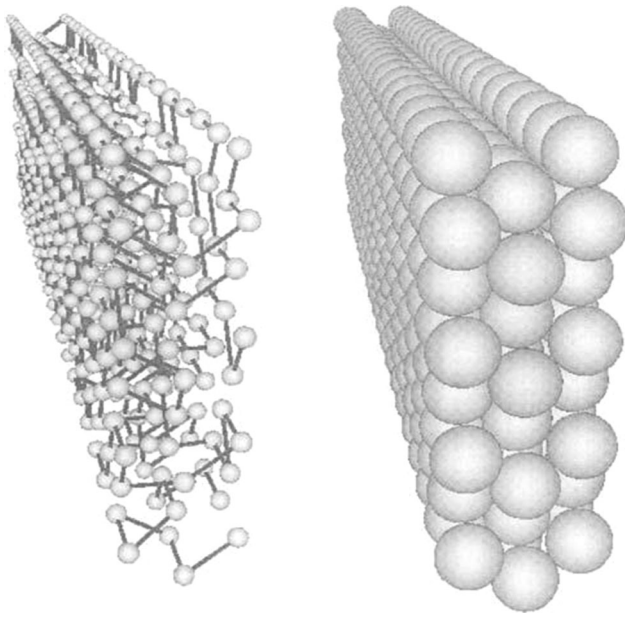

Figure 1 Model of computer-generated material mimicking a typical polymeric coiled macromolecular chain structure. In the *left visualization*, we show small statistical segments diameters to display the coiled chain structures (chemical bonds between segments); in the *right visualization*, the segments have the actual diameter corresponding to the typical final packing of the CGM.

While this situation prevails, most of effort in the field of PBMs is concentrated on improvement of mechanical properties [9–11] and relationships between those properties and phase structure [12–14]. In some cases, dielectric properties are also important [15]. In turn, when one now focuses on tribological properties of PBMs only, one finds that large information is provided for specific materials [7, 8], with less effort on general understanding of polymer tribology.

Such understanding can be provided by computer simulations [16], as discussed in a review article [17]. Since the publication [17], the use of PBMs has still grown significantly because of their relative inexpensiveness and ease of manufacturing. Previous literature has documented the phenomenon of scratch resistance for a variety of materials, largely on the basis of experimental data. In the present work, we focus on sliding wear of polymers, analyzing the effect of different parameters on the response of the material. Thus, the present work is important not only for the improved understanding of the phenomena related to scratching and wear, but clearly has also economic implications as a step towards developing materials with improved tribological properties.

Computational research is a growing field that offers several advantages over traditional, physical experimental research. One can vary parameters one at a time; for instance, in varying temperature in experiments on materials, one unavoidably varies simultaneously the free volume. In the case of simulation of scratch resistance testing, computations allow us to examine nanoscale scratches with precision, and also allow for extreme external conditions such as high temperatures and pressures—usually difficult or even impossible to realize in a laboratory. Simulations can also serve as a strong validation of existing experimental phenomenon, such as strain hardening in polymer sliding wear [18]. Despite the host of advantages, simulations remain a small portion of materials research—especially in the field of polymer scratch resistance.

We have used the classical molecular dynamics (MD) method created by Alder and Wainwright [19], and then discussed by Fossey [20]. One determines the evolution of the interaction of particles (molecules, or atoms, or ions, or polymer chain segments) over time by integrating their equations of motion; the equations are provided below. Using three-dimensional vector positions and Newton's second law of motion, we are able to calculate time-dependent displacement values of any particle. Importantly, molecular dynamics takes intermolecular forces into account. As part of a triangular lattice, each particle has up to twelve nearest neighbors (exceptions from vacancies in the lattice), with which interactions are calculated. In the triangular lattice, all nearest neighbors of a given particle are identical—in contrast for instance to the square lattice. The temperature of the simulation is kept constant, namely at room temperature.

We conduct MD computer simulation on a model of high-density polyethylene (HDPE). In comparison to abrasive wear, sliding wear shows better reproducibility [21]. An exhaustive literature review found no computer simulations of sliding wear. In this study, we focus on analyzing the effects of force size and indenter diameter on the penetration (instantaneous) depth R_p and recovery (healing) depth R_h of polymer segments. The percentage of material recovery, denoted as φ, is obtained from the two previous variables using the following equation:

$$\varphi = (R_p - R_h)100\%/R_p. \quad (1)$$

Table 1 Interaction potentials parameters used

	Type	α (kJ/mol)	β (nm)	R_{cutoff} (nm)
Intramolecular bond	Primary (covalent)	334	40	70
Intermolecular bond	Secondary	0.63	44	77

Table 2 Combinations of force magnitudes and diameters used in sliding wear simulation

Force magnitude (nN)	0.3	0.3	0.3	0.5	0.5	0.5	0.7	0.7	0.7
Indenter diameter (nm)	147	245	343	147	245	343	147	245	343

Note that exceptionally two more diameters (196 and 441 nm) were employed (Fig. 4, "Results and discussion section"), but only for the 0.7 nN force level, to expand the typical range of diameter values

Material generation

In Fig. 1, we show the type of structure of the computer-generated materials (CGMs) used in simulations (although a very small CGM is shown for perspicuity sake). On the left, one can see the primary bonds between segments along the polymeric chains with segments shown as small spheres. Thus, connectivity of the segments in chains is seen. On the right, each segment is represented by a sphere. We employ the coarse-grain model, which groups clusters of atoms into a single segment. When calculating the intermolecular and intramolecular forces, the segment is treated as if it were a single particle. There are circa two hundred C_2H_4 monomers assumed within a single statistical segment (each sphere represents a statistical segment in Fig. 1). The concept of the statistical segment has been advocated in particular by Flory [22]. Our program generates a material from unconnected statistical segments, later bonding them sequentially into self-avoiding coiled chains that represent a purely amorphous high-density polyethylene (HDPE) material, and also because a body of experimental data is available. We use HDPE as the material for simulation primarily because its simple structure serves as the basis for more complex polymers and polymer composites. The approach employed in our material generation program is described further in detail in an earlier paper [23].

Interactions and forces

Scratching simulation uses the intra- and intermolecular potentials of HDPE to calculate the forces on the individual segments. We use the Gustav Mie potential, developed in 1903 [24] and later appropriated by Sir John Lennard-Jones [25]:

$$U(r)_{\text{intra/inter}} = 4\alpha\left[\left(\frac{\beta}{r}\right)^{12} - \left(\frac{\beta}{r}\right)^{6}\right], \tag{2}$$

where U(r) is the bond energy as a function of the bond distance r, α is the potential well depth, and β is the value for which U(r) is zero (the collision diameter). The forces acting on the bodies resulting from the interactions are as follows:

$$F(r) = -\frac{\mathrm{d}U(r)}{\mathrm{d}r}. \tag{3}$$

The total force acting on each segment comes from the sum of all the neighbor potentials and the external scratching force produced by the indenter. Thus,

$$F_i^{\text{total}} = \sum_{i}^{\text{intra/inter}} -\frac{\mathrm{d}U(r)}{\mathrm{d}r} + F^{\text{ext}}, \tag{4}$$

where F_i is the force on segment i, and the summation includes all inter- and intramolecular forces, while F^{ext} represents the external scratching force. Values used in the simulations are shown in Table 1 (determined in earlier work of MD tensile behavior simulations).

Using these values, we can calculate the energy potential for each time step. If $r \le r_{\text{cutoff}}$, one uses Eq. (4) to calculate $U(r)$. However, if $r > r_{\text{cutoff}}$, $U(r) = 0$.

Sliding wear simulations

Our sliding wear test consists of 15 consecutive micro-scratches, similar to what one does in experimental sliding wear tests [5]. For each scratch, in order to mimic the interaction between a physical indenter and the material, an external force is applied perpendicularly to the top surface of the material and moved linearly along that top surface until it

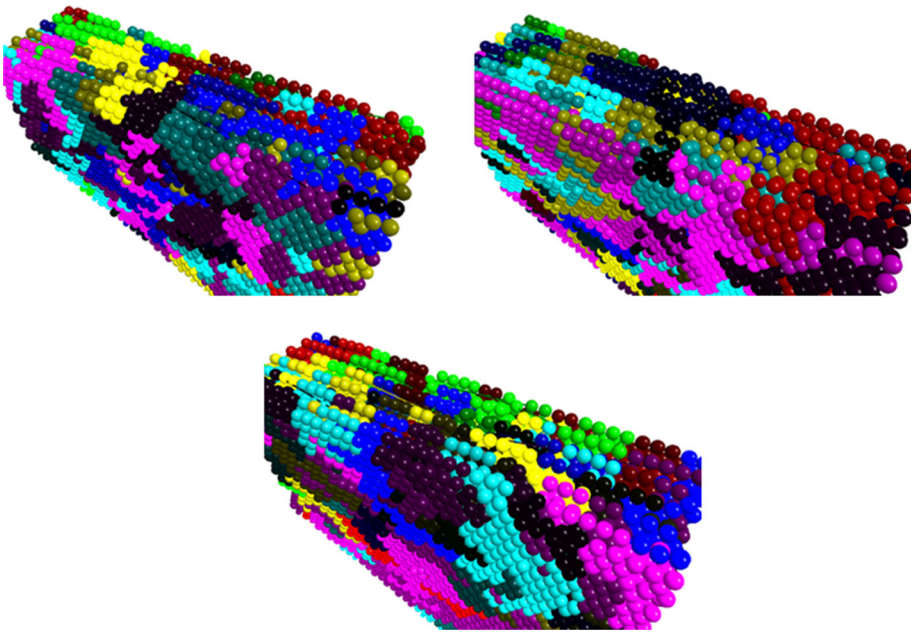

Figure 2 Examples of materials studied by simulation, with different polymeric chains represented in *different colors*.

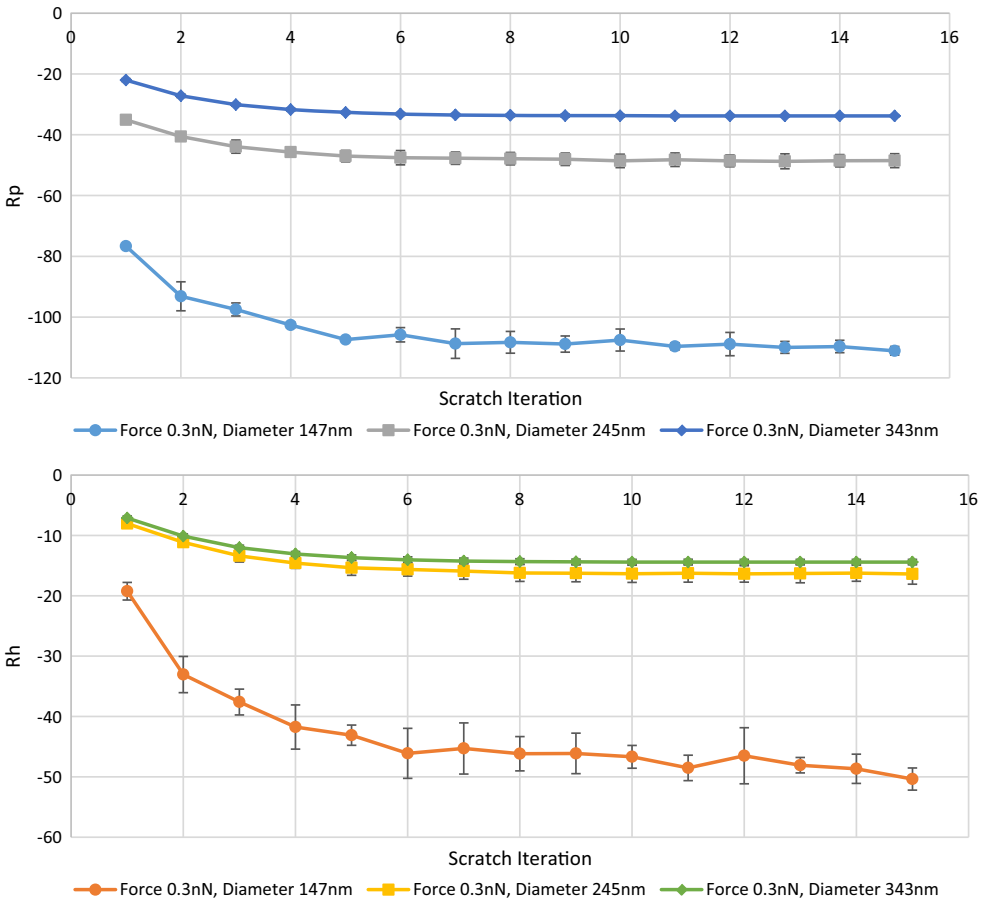

Figure 3 Average penetration and recovery depths in sliding wear determinations for 15 scratch runs for the force level of 0.3 nN.

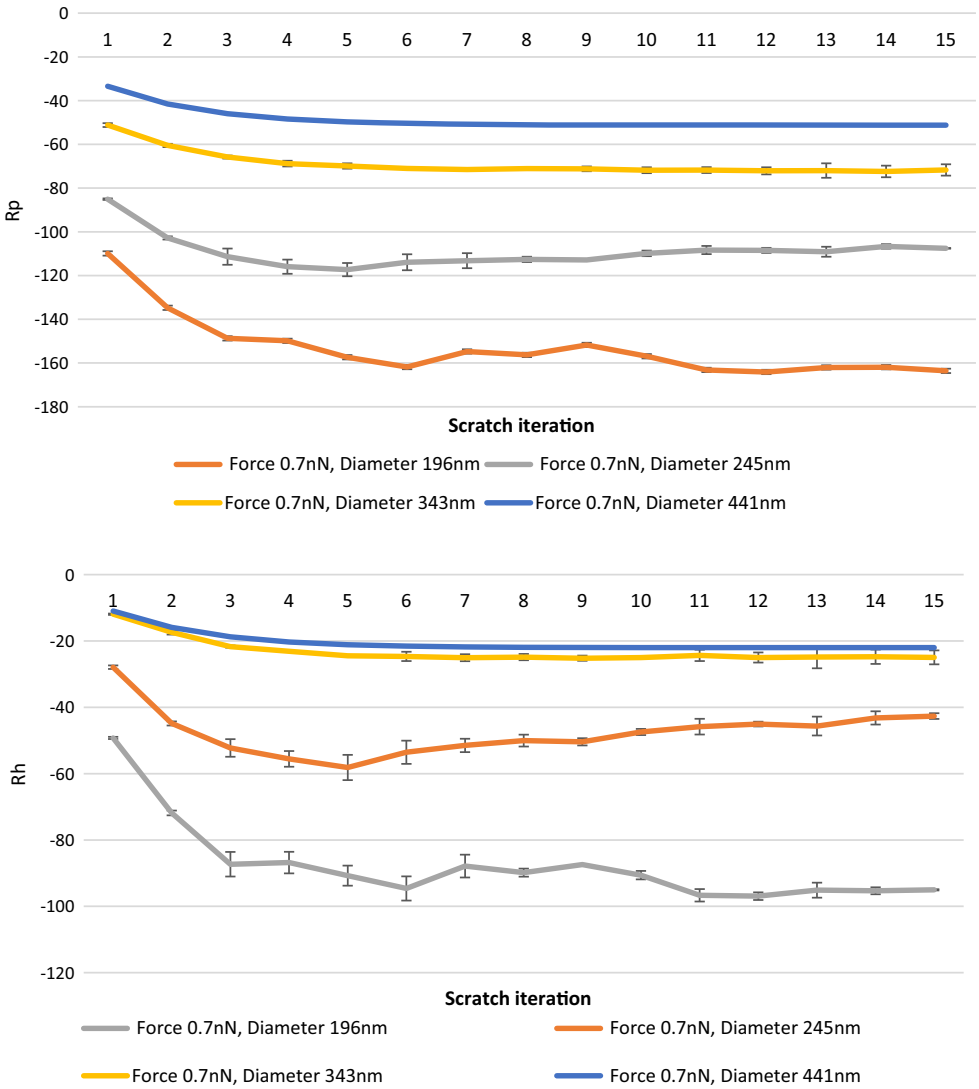

Figure 4 Average penetration and recovery depths in sliding wear determinations for 15 scratch runs for the force level of 0.7 nN.

approaches the opposite edge; some segments are left unscratched at both ends to avoid edge effects. The scratch progress is monitored for every time step, but only recorded every 2000 time steps—the time required to reach a quasi-equilibrium state on that iteration. The applied force is divided evenly among the segments being scratched at that particular time step. The penetration depth R_p is the averaged positions of the impacted segments when they are directly under the indenter. After the scratch has been completed, the indenter force is removed, and we allow 80 simulation iterations (of 2000 time steps each) for the scratched surface to recover without any external forces applied. This allows the viscoelastic nature of the material to manifest itself in healing, or recovery, seen as decreasing the depth of the groove—as it does in experiments as well. We record the recovery depth R_h so obtained. The 80 simulation iterations were found sufficient for the recovery to reach a plateau corresponding to less than 1 % change in segment positions between iterations. The R_p value will be taken by first finding the R_p of each segment in the scratching path, and then averaging these numbers. The same applies for R_h. To gather a variety of data, we conducted nine sliding wear simulations by varying two parameters, namely the force and the indenter diameter; see Table 2.

The CGM used for these simulations was HDPE with simulation cell size of 1.75 μm width, 0.6 μm height, and 2.0 μm length. We generated three different material configurations with the same size (due to the random nature of the generation process, each time it leads to unique macromolecular chain conformations), and for each material, we ran the set

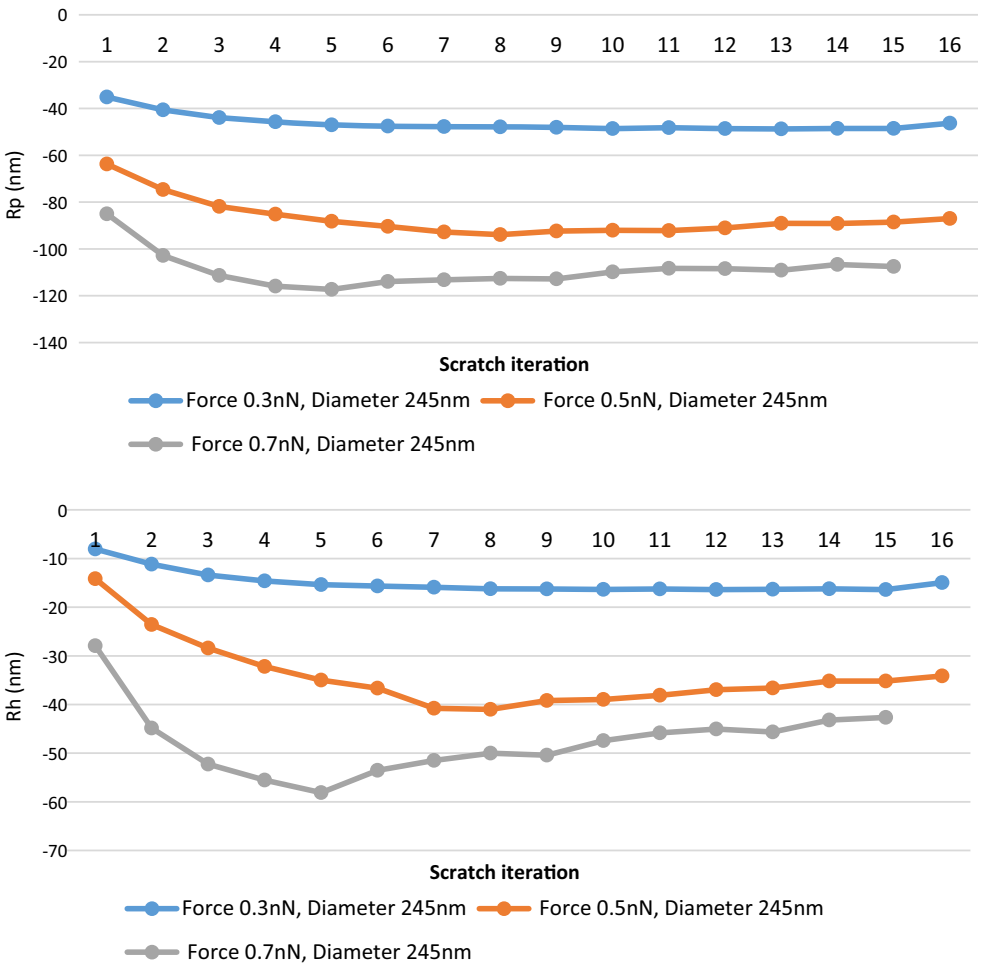

Figure 5 Average penetration and recovery depths in sliding wear determinations for 15 scratch runs.

of sliding wear parameters, as displayed in Table 2. Figure 2 shows an example of three different materials, created with the same input parameters, where colors represent the individual chains. We call these materials A, B, and C, respectively. We then consider the average sliding wear data of the three materials, to ensure representativity of the results, and thus we expect this approach to unveil accurate results.

Validation

As with any simulation work, results must be reviewed for validity before drawing conclusions. With experimentation on tangible materials, this validity is rightfully assumed. However, simulation work is often questioned, especially when the success of such work is dependent on realistic models. Therefore, we show how, despite the necessary simplifying assumptions, our model can effectively reproduce key behaviors and properties.

Experimental sliding wear results obtained with a micro-scratch (MST) tester for several polymers and reviewed in [5] will be referenced as evidence of simulation validity.

In addition, we can further justify our simulations theoretically through a set of assumptions. The first of these is that the molecular dynamics model we employ is an accurate representation of the polymeric systems under study. There is evidence for this assumption since molecular dynamics is a well-established method to analyze the dynamic behavior of a material over time. The Mie potential that we use is known to properly model the interactions between HDPE molecules. Our theoretical material has physical properties similar to the material we are trying to model. When we generate our material, we account for the non-crystalline characteristics of purely amorphous polyethylene through a randomization of chains during the creation of our material. In addition, we allow for a period of equilibration after

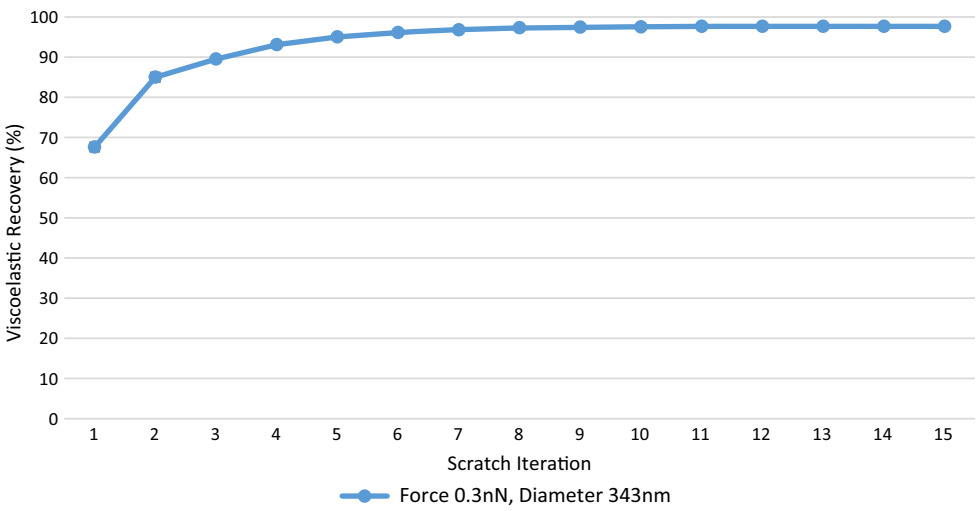

Figure 6 An example of a viscoelastic recovery diagram.

generating our material, letting the material reach a quasi-equilibrium state before applying any external forces. Using these assumptions, one can plausibly infer that our simulations of model HDPE are reliable and valid.

All materials were allowed for a full recovery after sliding wear. We define full recovery as when the percent change of penetration depth from one iteration to the next is less than 1 %.

Results and discussion

In Figs. 3 and 4, we show the effect of the indenter diameter on R_p and R_h values for each scratch in the sliding wear simulation; the first figure pertains to the force of 0.3 nN, the smallest we have used (below this the deformations are almost negligible), and the latter pertains to the force of 0.7 nN, the highest we have used (above this value, we obtain significant chain rupture and excessive displacement which would start exhibiting simulation limits artifacts such as edge effects). As our CGM (and the respective indenter contact area) size is significantly smaller than in the experiments, the forces employed act proportionately on a smaller scale than those typical of experimental testing. Each data point corresponds to the average values from three different CGMs (the same input parameters, but different chain configurations, as these result from the random nature of the material generation procedure), and include the standard deviation at each data point. The standard deviation value is representative of the degree of variation of the results gathered from the three materials. For the 0.7 nN force trials, we also ran simulations with indenter diameter of 196 and 441 nm; we show these results in Fig. 4.

We see in Figs. 3 and 4 that in all cases we observe decreased penetration and recovery depths as the indenter size is increased. This is due to the increased force per unit area at smaller indenter sizes. One can also notice a trend as the force increases; the material exhibits larger penetration depth, and it is clearly not a linear trend. The same statement applies to the recovery depth.

We also see strain hardening in sliding wear determination discovered experimentally in 2004 [18]—one more validation of our simulations. The polymer develops resistance to further wear over the course of the scratch runs. Experimentally, it was found that vertical indentations are deeper on the flat surface surrounding the groove than inside the groove [26]; apparently, densification inside the groove takes place.

Interestingly, we also observe that standard deviations are higher for the smaller diameters and higher forces. This could be expected, as scratches go deeper into the material, more variation appears between CGMs with different chain configurations (it hardly affects very shallow scratches, but affects significantly deep ones, where segments are displaced and sometimes the indenter force even leads to local chain rupture).

Although this larger influence on the specific chain conformation under the indenter for higher forces has implications to the resistance the material offers to being scratched, the gap between curves is much larger than the standard deviation, keeping the

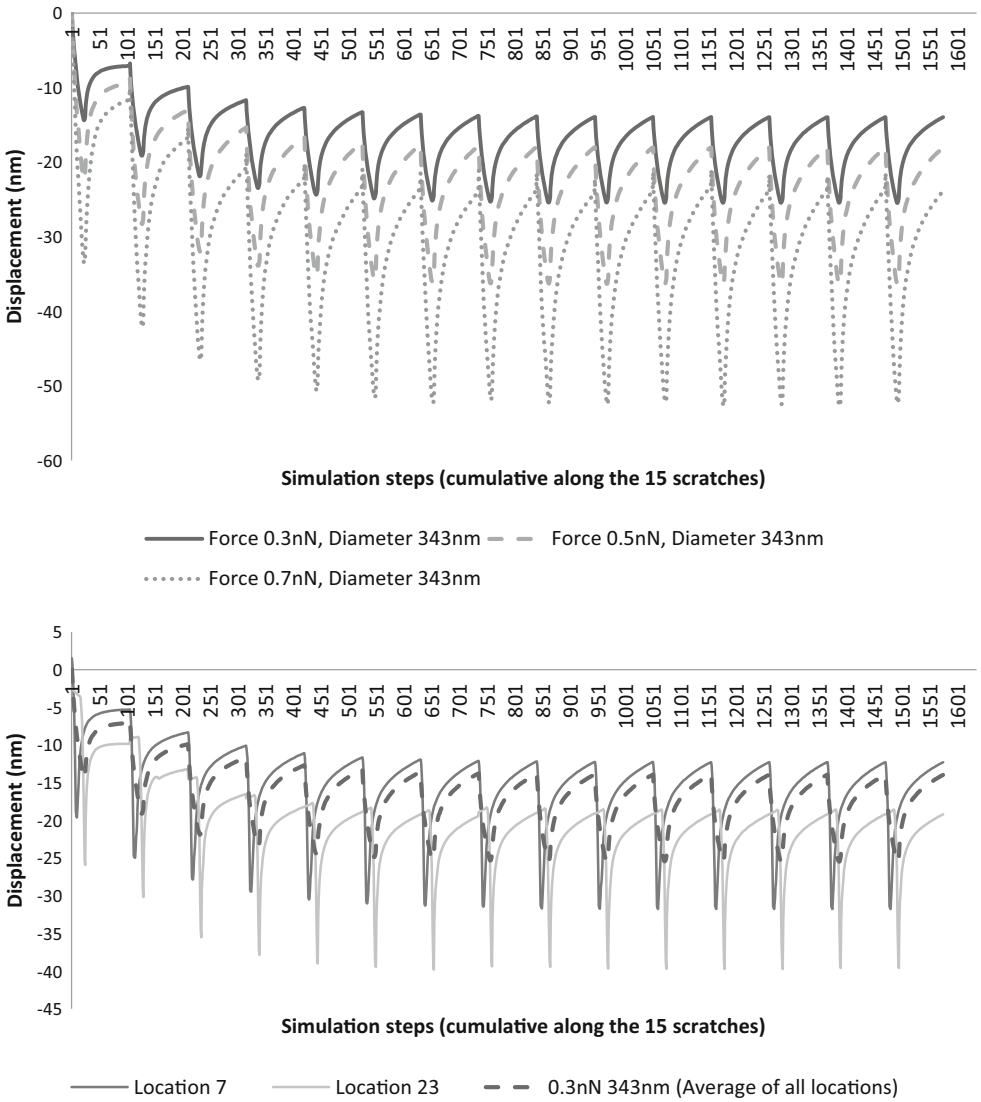

Figure 7 Examples of displacement as a function of time diagrams: **a** comparison between the different force levels tested with the 343-nm indenter (average of all scratching path locations); **b** behavior at two locations along the scratching path, and average of all scratching path locations for only one of the simulation conditions of part (**a**).

trends perfectly clear. The relatively small standard deviation values overall reflect the accuracy of our results, and the reproducibility of the observed effects for any specific chain configuration of the CGM.

We have also used these same results to show the effect of the force magnitude on the penetration and recovery levels of the material. Figure 5 shows the effect of various force levels with a constant indenter diameter of 245 nm.

As expected, we see in Fig. 5 that an increase in force magnitude results in increased penetration and recovery. The strain hardening effect (as could be expected from what is known experimentally) is more significant for higher force levels.

In Fig. 6, we provide an example of calculation of the viscoelastic recovery φ calculated from Eq. (1).

In Fig. 6, we observe a lower viscoelastic recovery (φ) in early runs, which then increases up to almost 100 % values in later runs (note that for high force levels or smaller indenter diameters, the trend would be similar, but the φ values lower). An explanation for this can be densification inside the groove, as discussed above.

Note that the recovery % for each scratch is relative to the position of the segments immediately before the scratch takes place.

As claimed before, simulations have at least one key advantage compared to experiments: we can follow the response of the material in extreme detail, even at a molecular level (usually more than can be scrutinized and reported). In Fig. 7, we show two diagrams of displacement as a function of time, with the full profile on penetration and recovery.

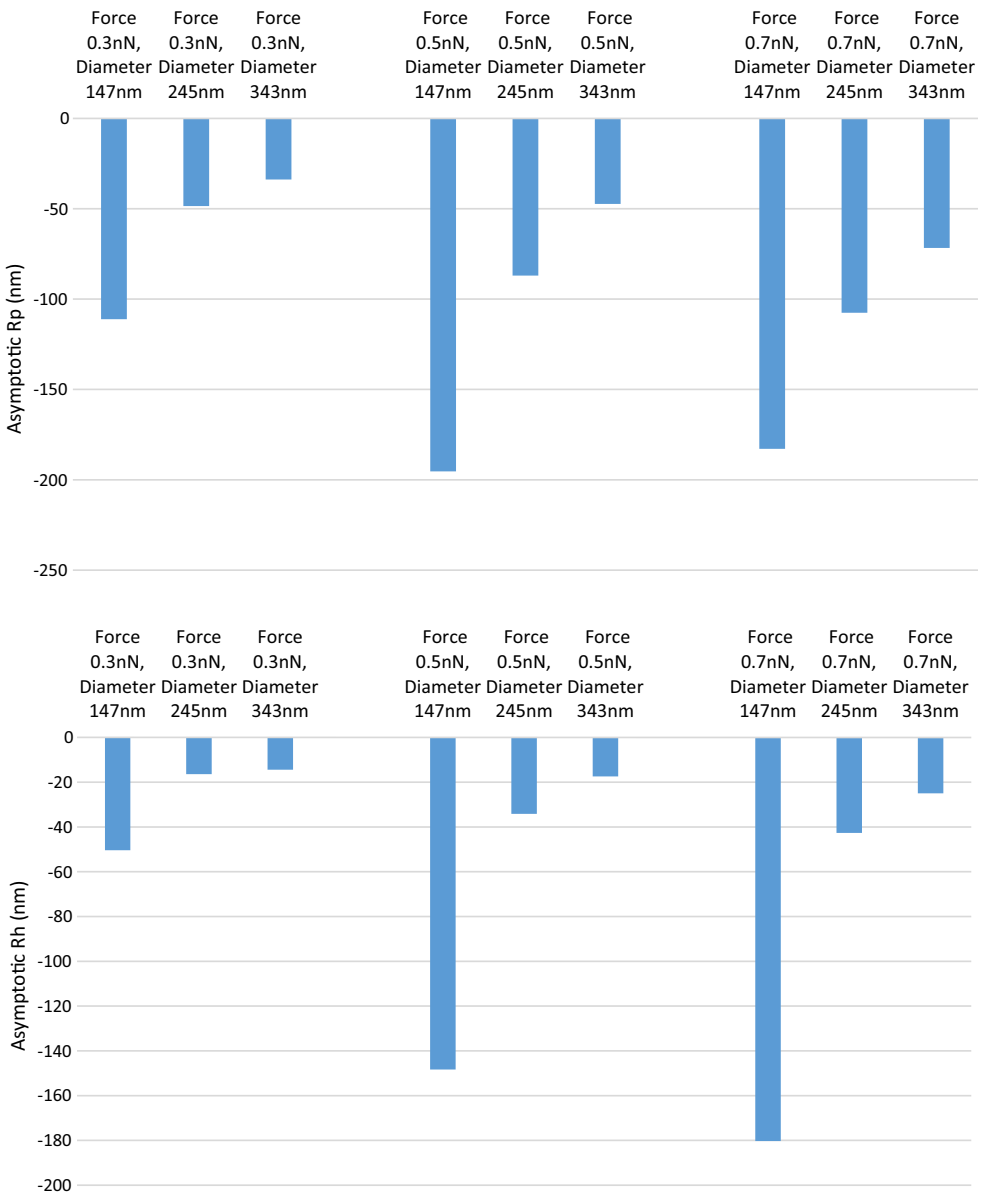

Figure 8 Asymptotic R_p and R_h values for all simulated conditions.

In Fig. 7a, we see the successive penetration and recovery cycles for all 15 scratches in sequence. This is the cumulative response of the vertical displacement of the scratch path along the 15 scratches, given that we have 104 total simulation steps for each scratch (24 simulation steps of the scratch itself, which comes from the length of the top surface of the material which is where the scratch occurs, plus 80 of subsequent recovery of the material with no external forces applied). We notice that as the number of scratch iterations increases, the viscoelastic recovery value becomes asymptotic (this has been shown in more detail for one case in Fig. 6). Location 7, which is one of the first locations on the surface of the material to get scratched, penetrates earlier than location 23 (obviously, as the indenter moves along the scratch path), and earlier than the average of all locations (equally obvious). The profiles for location 7 are similar to location 23, but with shallower depths overall. We had in a previous publication [20] identified an effect we termed the "crooked smile" topography of a scratch, and which results from the unscratched edges to the left and to the right of the scratch path. Those edges provide lateral support to the segments near the ends of the scratch path. Thus, that effect is also seen here.

In Fig. 8, we compare only asymptotic R_p and R_h values after 15 scratches, to provide a different

perspective on the effects we observed for the scratching force and indenter diameter parameters.

We see in Fig. 8 that, consistently, the magnitudes of R_p and R_h decrease as the indenter diameter increases. As already noted, this is expected as an increased diameter means less force per unit surface area, and hence decreased penetration and less recovery. As the force magnitude increases, penetration and recovery values increase in magnitude. This means that increased force results in increased displacement on the surface of the material.

Concluding remarks

We have employed computer simulations to study the scratching behavior of an HDPE computer model with classical MD, namely under multiple consecutive scratches along the same groove. This is analogous to sliding wear experimental tests.

From the results, we can clearly observe that increasing the scratching force or decreasing the indenter diameter leads to higher penetration depths and lower recovery depths. Furthermore, it is not a linear increase, but becomes increasingly more pronounced. As for sliding wear, we have concluded that the first half a dozen or so scratches exhibit diminishing effects, and then the properties tend to an asymptotic response. This is analogous to a strain hardening or densification effect, and it varies slightly depending on the scratching conditions.

After each scratch of a sliding wear simulation, the material recovers partially in a significant and quick manner—like a viscoelastic material should—and then more slowly until the depth stabilizes at the recovery depth. Moreover, after some scratches, recovery percentage also tends to an asymptote, which can be close to 100 % for relatively low forces or high indenter diameters.

Our simulations of scratching behavior of polymeric materials provide much more information than experimental testing alone, and should be used synergically with experiments.

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