

Simulating scratch behavior of polymers with mesoscopic molecular dynamics

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HIGHLIGHTS

- ▶ Experimental scratch resistance testing provides only 2 values for a material.
- ▶ Our simulations provide a continuous dependence on time of the segment depth on the path of the indenter.
- ▶ Effects of indenter force and size have been determined.
- ▶ We discuss a "crooked smile" effect on scratched surfaces and the reasons for its appearance.

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ABSTRACT

Part replacement and repair is needed in structures with moving parts because of scratchability and wear. In spite of some accumulation of experimental evidence, scratch resistance is still not well understood. We have applied molecular dynamics to study scratch resistance of amorphous polymeric materials through computer simulations. As a first approach, a coarse grain model was created for high density polyethylene at the mesoscale. We have also extended the traditional approach and used real units rather than reduced units (to our knowledge, for the first time), which enable an improved quantification of simulation results. The obtained results include analysis of penetration depth, residual depth and recovery percentage related to indenter force and size. Our results show there is a clear effect from these parameters on the tribological properties. We also discuss a "crooked smile" effect on the scratched surface and the reasons for its appearance.

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1. Introduction

Tribology is the study of friction, scratchability, wear – and also of methods mitigating these effects such as by lubrication. In 1966, Henry Peter Jost coined this term in a report to the British Government [1], estimating that millions of pound sterling are spent every year replacing parts and repairing equipment due to the consequences of friction, wear and corrosion. Indeed, wear is a common, and costly, problem, as Rabinowicz later stressed in his book [2]. Wear occurs when two materials rub against one another. Engineers must analyze wear with great scrutiny to be able to

mitigate the effects. Polymer-based materials (PBMs) are especially subject to breaking down from wear due to their relative softness – while PBMs are often used in applications that are susceptible to wear such as surface coatings or polymer based composites. We note that wear and scratchability of polymers and polymer-based composites cannot be mitigated by liquid lubricants as it is typically done for metals. Liquid lubricants are apt to be absorbed by polymers – causing swelling.

Scratch resistance is particularly important for polymeric materials; research has shown that a scratch may acquire the role of a crack and become the origin of crack propagation [3]. The importance of tribological properties, and in particular scratch resistance, has also been noted in our previous work [4]. Since then, the use of PBMs has still grown significantly because of their relative inexpensiveness and ease of manufacturing. In the present work we focus on the scratching behavior of polymeric materials, analyzing the effect of different parameters on the response of the

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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 toward developing materials with improved tribological properties.

Computational research is a growing field that offers many advantages over traditional, physical experimental research [5]. Compared to experiments, one can achieve considerable savings in time and cost, if conducted in an effective manner. Even more important advantage of computer simulations is the ability to obtain information that is not readily available experimentally. Simulations give us the capability to deal with a variety of environmental conditions such as: very small scales, very high temperatures or pressures that are otherwise difficult or impossible to implement experimentally. A simulation can provide a number of properties, such as the use of the embedded atom model in calculating properties of nickel [6]. Combinations of experimental and computational techniques are possible, such as calculation of thickness and refractive index of thin films and comparing them with experimental results [7]. Despite the advantages, computational research still represents a small percentage of the total research done – while it presents considerable potential for the future.

We have used the classical molecular dynamics (MD) method as developed by Berni J. Alder and collaborators at the Lawrence Livermore Laboratory in the 1950's [8]. With MD, one studies the motion of particles (atoms, molecules, or else polymer chain segments) solving Newton's equations of motion. Thus, laser ablation has been studied by Horiuchi and coworkers [9]. Chaban and Nazarenko, respectively in Rochester, NY and in Harkiv, studied structure and strength of composites of the graphite + carbon nanotubes type [10]. Applications of the MD method to polymeric materials have been reviewed before [5,11–14].

There are some inherent challenges with using MD, or any method of computer simulation, on polymeric materials, as Binder discusses in detail [11]. Metallic materials are crystalline; it is much easier to create a monoatomic lattice on a computer than to create a polymer, even if in the latter case one starts from monomers on a lattice [15]. Polymeric materials, which consist of long chains interweaving between one another, make the use of the MD technique more challenging. There have been simulations of polymers or polymer-based composites, but for purposes other than ours. Van der Giessen and coworkers used first continuum and constitutive models to investigate crack tip fields [16] and crazes [17] in glassy polymers, but then MD to study self-diffusion in polymer melts [18], glass transitions [19], as well as pull-out and adhesion [20,21].

Simulations dealing with scratch and wear resistance commonly deal with crystalline materials; one such report simulates scratch resistance on single crystal aluminum [22]. As expected, under an application of a load, the scratch groove can become a crack and propagates. The propagation occurs along crystallographic planes and grain boundaries, as would be expected. Since in polymeric materials crystallographic plains and grain boundaries do not exist, crack propagation has to occur in a different fashion than in crystalline metals.

Another property of polymeric materials that separates them from metals and ceramics is that they are viscoelastic: their response exhibits both elastic and inelastic components and depends on time. Thus, when a polymeric material deforms, it should recover a portion of this deformation.

With micro-scratch experiments one obtains information in two forms: the penetration depth, R_p , and the residual, also known as healing or recovery, depth R_h [23–25]. R_p is the instantaneous depth at the moment when the indenter has hit a given location and R_h is the depth of the material after it has had time to recover.

Besides these two parameters, the only other method of analysis used in experiments is with images taken of the tracks with SEM microscopes or with optical microscopes [26–28]. Computer simulations have the capability of being able to provide the depth of every segment over time, instead of only the status before and after scratch. In this work R_h was determined after exactly 30 iterations since the time the indenter was applied to that surface location (thus, always a constant recovery time). The percentage of recovery φ is obtained from the two previous variables, namely as

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

2. Model

The principle of MD is simple: one solves Newton's equations of motion (force equals mass times acceleration) for the interacting many-body system numerically on a computer. In general, the particles may represent any physical entity that can be defined by a set of interaction potentials. In the employed model, each particle represents a set of C_2H_4 monomeric units – a coarse grain model of HDPE. If $u(r)$ is the total potential between two particles i of mass m_i and position $R_i(t)$ at time t , the pertinent equation is:

$$m_i \left(d^2/dt^2 \right) r_i(t) = -\nabla u(R_i), \quad i = 1, 2, \dots, N \quad (2)$$

MD has been used to study several classes of properties, including mechanical [5,11,29–32], dielectric [33] and electrical [34] properties and diffusivity [35]. For that matter, diffusivity was also studied with the Monte Carlo simulation method [36–38]. MD can be used to simulate single atoms or molecules, using what are termed atomistic or united-atom models. However, with the use of the statistical segment concept introduced by Paul J. Flory [39,40], MD can also be used at the mesoscale to study larger systems [5,41–47]. This while Brownian Dynamics seems to be more suitable for simulating polymer solutions, at rest and in flow [48,49].

To improve perspicuity of our results, we have associated the parameters of the model with units on a real scale. This should enable quantitative assessments in addition to qualitative ones – and thus facilitate comparison with experimental data.

To use real units, our material is modeled after the interactions present in high density polyethylene (HDPE); as mentioned before, each statistical segment representing a set of C_2H_4 repeating units in the HDPE chain. HDPE is a commonly used model in polymer simulations [45–47] because of its simplicity; the intersegmental interactions have been well studied by chemists [50–52]. To represent interactions between the statistical segments we have used the pair (6, 12) potential defined by Gustav Mie in 1903 [53], namely

$$u(r)_{\text{intra/inter}} = 4\epsilon \left[(\sigma/R)^{12} - (\sigma/R)^6 \right] \quad (3)$$

More than 20 years later John Lennard-Jones started to use the Mie potential [54] – the reason why often the name Lennard-Jones or L-J potential is used. $u(R)$ is the potential energy acting between the two particles (in our case statistical chain segments) as a function of the interparticle distance R , ϵ is depth of the potential well (the minimum on the $u(R)$ diagram) and σ is the value for which $u(R)$ is 0 (the collision diameter at which the attraction and repulsion forces are equal). As already noted, our parameters used in Eq. (3) are based on the literature [50–52]. During simulation, the forces acting on the bodies resulting from pairwise interactions are calculated as:

$$F(r) = -du(R)/dR \quad (4)$$

The total force acting on a segment results from interactions with its neighbors according to Eq. (4) plus an external force F^{ext} :

$$F_i = \sum_i \{ -(du(R)/dR) \} + F^{\text{ext}} \quad (5)$$

Here F_i is the force acting on segment i , $\sum_i \{ -(du(R)/dR) \}$ is the sum of all the inter-chain and intra-chain forces from the neighboring segments, while in our case F^{ext} is the external scratching force applied on surface segments in the path of the indenter.

For the simulation, further assumptions have been made, namely a locked bottom surface and a virtual bonding box. The set of segments on the bottom surface (lowest position along the Y-axis) is locked, to prevent them from moving in any direction. This stops the entire material from simply displacing vertically under the external scratching force and can be thought of as the surface or substrate on which the material is placed for testing. Precaution must be taken to ensure that this bottom surface is at a sufficiently large distance away from the segments being scratched on the top surface so that this does not affect the results. Similarly, virtual boundaries along the 4 lateral surfaces (perpendicular to the applied scratching force) are introduced. This effectively creates a bounding box that only prevents the material from flattening out during the scratching process. When a segment attempts to move past this bounding box, it is simply not allowed to go further than the virtual wall. This is akin to simulating a small section of material in the bulk, or a constrained scratch where the material is inside a small container. Similarly to the issue of the locked segments on the bottom surface, the indenter is kept several segments away from the lateral edges, and we have tested materials with different sizes to ensure there is no edge effect on the results.

MD simulations use time steps (the smallest discrete interval that can be defined), and iterations or loops (each consisting of a certain number of time steps). Each time step is considered as dt in Eq. (2), and is the size of each step the simulation runs: i.e., after each time step the coordinate positions of every segment are calculated. For these simulations, each time step corresponds to five pico seconds: $dt = 5$ ps, that is considerable larger than typical MD simulations which are often on the femtosecond range. This is achieved because of the larger coarse-graining used with these simulations; one segment represents on the order of a couple of hundred C_2H_4 monomeric units. One iteration consists of 2000 time steps, and after each iteration, output files are produced for analysis. A typical simulation goes through 50 to 100 iterations; e.g., one simulation can be around $2 \cdot 10^4$ time steps.

Time integration was performed using a leap-frog algorithm [55]; we considered it preferable to the also often used Verlet algorithm [56] since scratching was performed at relatively high speed and the leap-frog variant handles velocity better. To avoid the effect of stochastic thermal forces, simulations were performed at constant (room) temperature, as the thermal effect of the motion of the indenter was not to be considered. Constant temperature was maintained by coupling the system to an external bath, using the Berendsen thermostat [57].

An external force is applied to the top surface of the material to simulate scratching. This force moves along a pre-defined scratching path, namely following the center of the top surface. Also, several segments are left unscratched before the beginning and after the end of the scratching path, again to ensure we do not have edge effects. The scratching force is displaced only at each simulation iteration (at 2000 time steps). The number of segments considered being under the indenter, and to which the force is applied, depends obviously on the size of the indenter. Some segments may continue to be under the influence of the indenter while it is moving, depending on its size. The applied force is divided

evenly among all those segments being scratched at each time step. Initially, only the segments on the top row feel the effect of the external scratching force. After the scratching has been completed and the indenter removed, 30 additional iterations are performed to allow for the material to recover, an important step in studying the scratching behavior. We recall that in experiments for viscoelastic materials the recovery always takes place [4,14,58,59]; also see again Eq. (1).

3. Method

The simulation is broken down into three stages: material generation, scratching simulation, and data extraction and visualization. The first stage is accomplished with a program titled “Genmat”, the second with a program titled “Scratch”, and the third with two programs, one titled “Vis” and another titled “Measure”. Genmat generates the polymeric material through a polymerization process, described in detail in our own previous work [60]. Subsequently, the MD simulations program, Scratch, takes the data from Genmat then simulates the scratching forces on the material with MD. Scratch has also been used in earlier forms in previous work [4,14,60]. Modifications have been made to both programs to account for the real units of HDPE while the material size has been increased considerably.

The goal of these simulations is to identify and characterize trends in the dependence of the properties on the simulation parameters. Two parameters are tested: amount of force and size of indenter. Increasing the force should increase the R_p , and likely in a close to linear fashion. With larger indenter size (maintaining the total applied force constant), the force is spread over a larger number of segments, in effect creating a blunter indenter. This will likely result in an effective decrease in penetration, but what effects on recovery it could did not seem foreseeable.

Forces must be used that are sufficient to cause deformation but not as large so as to penetrate toward the bottom row, which would result in unreliable data. Forces are varied from 0.05 nN to 0.5 nN. Indenter size ranges from about the diameter of two segments, 98 nm, to about 5 segments in diameter, 245 nm. An indenter smaller than 98 nm will not have a sufficient number of chain segments being indented and more than 245 nm would be getting too close to the borders of the material (roughly 500 nm in total width) (Table 1).

4. Selected results

As mentioned before, the depth resulting from the indenter movement is measured over time. Two variables have large effect: the applied external force and the indenter size. Comparisons are through variations of force and indenter size.

Below are figures taking into account all of the data for a given material and summarizing the R_p , R_h and ϕ . This is done in two fashions, one by keeping the force constant and looking at it as a function of indenter size, in the other we keep the indenter size constant and consider the same parameters as a function of the applied force.

We first have a look at the top and one side of the material before, during and after a scratching simulation run. The results are shown in Fig. 1. In Fig. 1d we see the groove created by the indenter.

Table 1
Simulation parameters.

Material size	500 (width) \times 400 (height) \times 1400 (length) nm
Applied scratching force	0.05–0.5 nN
Indenter Diameter	98–245 nm

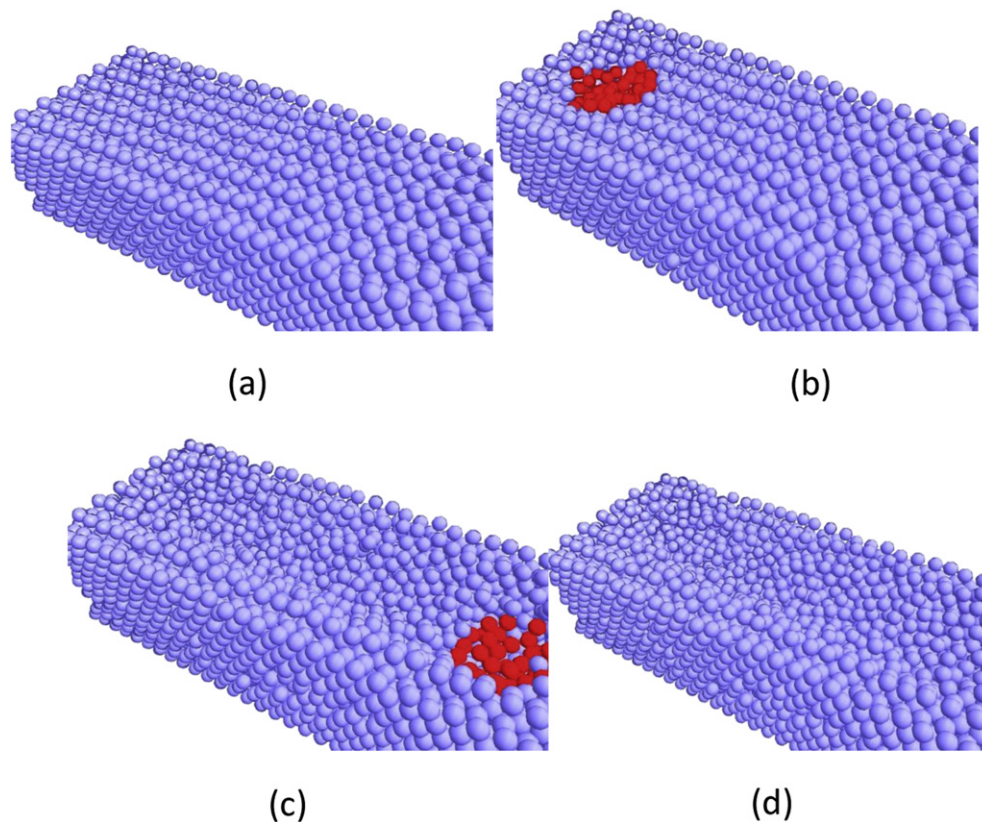


Fig. 1. Visualization of a material (a) before equilibrium, (b) during first force iteration, (c) during the last force iteration, and (d) after a recovery period.

In Fig. 2 we follow the depth changes with time along the path of the indenter, each line pertaining to a group of segments subjected to an indenter, such as the red clusters in Fig. 1b and c.

The same set of results can be looked upon from different points of view. Since each segment group has the penetration depth R_p (the minimum point on the depth vs. time curve in Fig. 2) as well as the recovery or healing depth R_h , we can plot these values as a function of location on the path of the indenter. The result for the same run as in Fig. 2 is shown in Fig. 3.

One way to look at Fig. 3 is to keep in mind that any surface – except for a perfect crystal – is neither atomically smooth nor flat. One recalls the first results of scratch resistance testing for a human

tooth [61]. Clearly there are locations along the groove created by the indenter where both R_p and R_h have larger absolute values than at some other locations; locations 11 and 19 in Fig. 2 are examples. In other words, the material itself will also affect the scratch resistance. Although every material is modeled with the same properties, there is one unique property for each material generated: chain spatial arrangement – which clearly affects the properties.

Since we have used several levels of force and indenters of several sizes, we can now consider effects of that size as a function of the force on the depths. The respective results for R_p and R_h are shown respectively in Figs. 4 and 5.

As expected, larger forces applied result in deeper grooves. As also expected, smaller indenter sizes result in deeper grooves; for a given level of force, a small indenter size means of course a larger

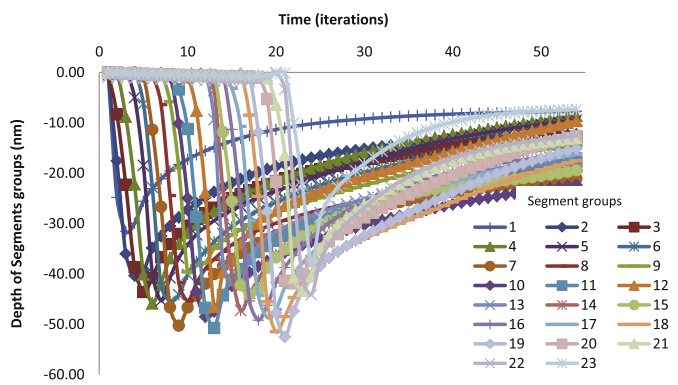


Fig. 2. An example of analysis program output. Each data point corresponds to the vertical position of a group of segments (those under the indenter at each iteration). The lines provide the profile of penetration and recovery. Segments shift downwards under the influence of the indenter, and then recover over time. The force level was 0.10 nN.

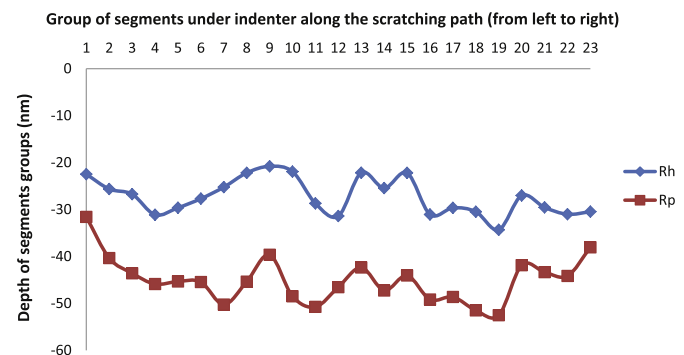


Fig. 3. The same simulation as in Fig. 2, this time showing the R_p and R_h of each group of segments.

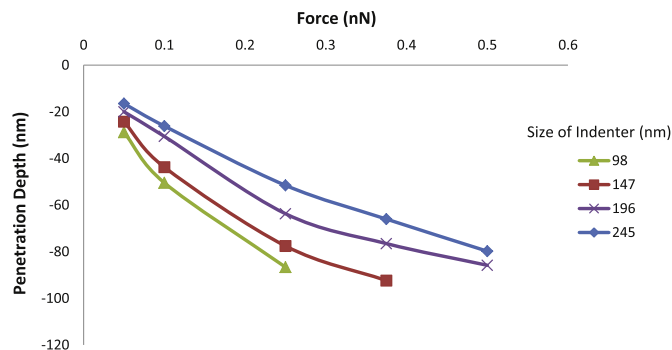


Fig. 4. R_p as a function of the external scratching force applied for Material One with four different indenter sizes.

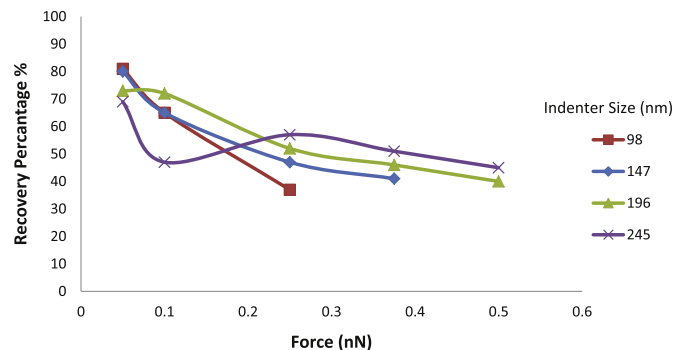


Fig. 6. Recovery percentage ϕ as a function of external scratching force.

force applied per unit area. In other words, a wider and thus blunter indenter distributes the force more uniformly, so overall the surface has a shallower residual depth. These results reinforce information available from experiments while they also show that the essential features of experimental scratch resistance testing have been captured by our MD simulation procedure. We further find there is no simple inverse proportionality between R_h and the indenter surface areas. Consider as an example results for the force of 2.5 nN in Fig. 5. We have $R_h \approx 57$ nm for the indenter diameter 98 nm. The surface area of the indenter (s) would then be equal to about 7500 square nm; $s = (98/2)^2\pi = 7543$ nm². With a larger indenter diameter of 245 nm, we have $R_h \approx 23$ nm and $s = (245/2)^2\pi = 47,144$ nm². However, $47,144/7543 = 6.25$. This while $57/23 = 2.48$. We infer that enlarging the surface area of the indenter results not only in lower force acting per unit area but also in a larger number of polymer chain segments collectively resisting the indentation.

We now consider the viscoelastic recovery defined by Eq. (1). A set of results pertaining to those presented in Figs. 4 and 5 is shown in Fig. 6. Except for two aberrant points in the beginning of the curve for the indenter diameter of 245 nm, we have in general higher recovery for larger indenter sizes. This seems related to the fact just discussed above: a larger surface area of the indenter "attacking" a polymer surface results in more chains resisting the attack.

We now consider our results in a still different way: penetration and residual depths as a function of indenter diameter for constant levels of force applied. The results for R_p are presented in Fig. 7 and for R_h in Fig. 8.

Figs. 7 and 8 confirm conclusions reached above: at a given external scratching force level, a larger indenter size results in shallower depth. This pertains to both the penetration and the

recovery depth. A fact we have not noted before: at higher external forces, the effect of blunting the scratching (shallower depth) by enlarging the indenter surface area is stronger.

5. General discussion

Intramolecular interactions between segments along any chain are much stronger than the intermolecular or secondary (van der Waals, dispersive or London) interactions. If a segment that is being indented by the external force is bonded to a neighboring segment on the top row that is not being acted on by the external force, the segment will penetrate less and recover more. This is one more effect that has been made clear by the simulations, an important one.

A clear way to see how the neighboring segments have an effect on R_p and R_h is what we have decided to call the "crooked smile"; see Fig. 9. The pattern is subtly visible in Fig. 3; the two ends of the scratch path are shallower than the middle. When a segment penetrates down due to the external force, it brings its neighbors (especially the intramolecular bonded neighbors) down with it. When a segment on the top row is not acted on by the indenter, it stays at the top and attracts its neighbors to stay there. The segments at the ends have fewer neighbors that are acted upon with the external scratching force.

The scratch occurs in a pattern with the second half of the curve being slightly deeper than the first half. This crooked smile pattern is an extension of the neighboring effect: the later segments have a small effect from all the previous segments that were acted upon along the scratching path. The leftmost neighbors to the first segments in the scratching path are never acted upon, and thus aid more noticeably the recovery of their neighbors.

LAPOM has a micro-scratch testing machine and has published papers on scratching polymeric materials [23–25,27,28] as well as

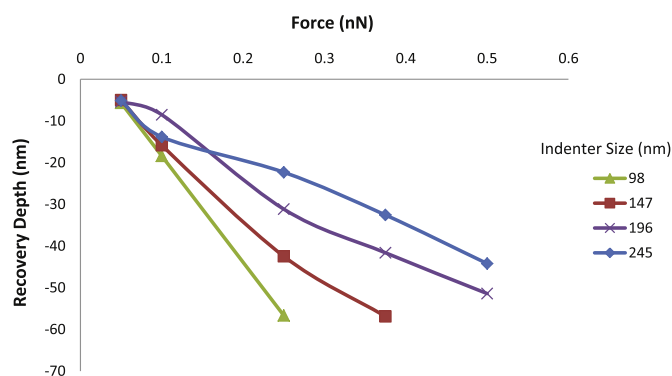


Fig. 5. R_h as a function of indenter size.

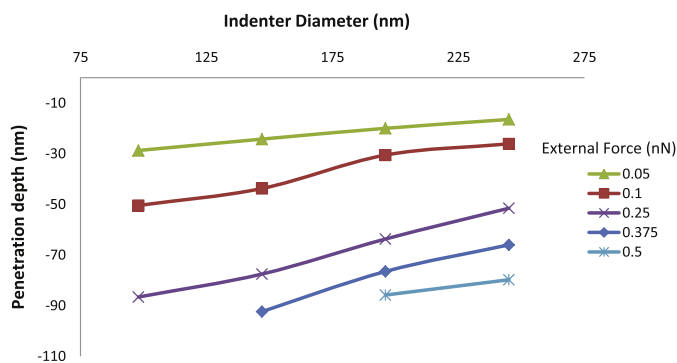


Fig. 7. Penetration depth in relation to the size of the indenter used. Five forces are used.

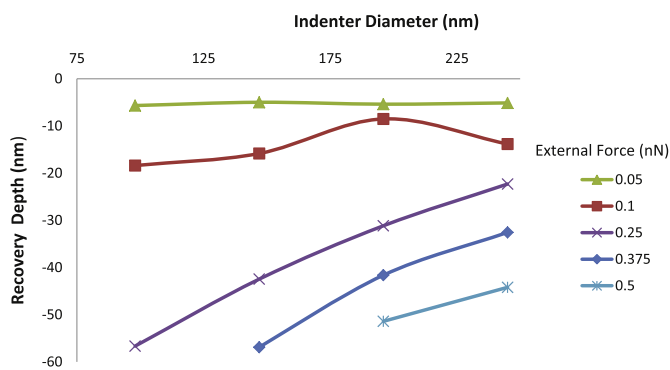


Fig. 8. Recovery depth as a function of indenter size.



Fig. 9. The crooked smile trend of a scratch surface.

metal pastes [62], during which R_p and R_h are measured. Two different types of tests are run, one with a constant force and one with an increasing force. Experiments with HDPE show that with for force of 5 N, R_p is about 50 μm while a force of 30 N results in $R_p \approx 450 \mu\text{m}$. The same experiments show an R_h of about 20 μm and 120 μm , respectively. These values correspond to φ of 60% and 73%. These tests were conducted with a micro tip indenter with a diameter of 200 μm .

In the present simulations we have used among others an indenter of 196 nm and a force of 0.1 nN. Our results are: $R_p = 31 \text{ nm}$, $R_h = 9 \text{ nm}$ and $\varphi = 72\%$. The diameter of the micro indenter is six orders of magnitude larger than the diameter used in the simulation and the force is ten orders of magnitude higher. While it is difficult to compare the values on so different scales, the percentage recovery φ is comparable, in fact quite close. We have not found experimental results for HDPE that would provide R_p and R_h values for HDPE based on using a smaller indenter size. Atomic force microscopy (AFM) techniques do come much closer to the nano- and micrometers scale [63]. However, they do not offer such data as R_p and R_h . With AFM, the type of deformation is analyzed with the use of scanning electron microscopy (SEM) as discussed by Dasari and Mishra [64]. An AFM machine can exert a scratching force from 1 μm up to 1 N. However, it is not possible to analyze the depth of the indenter over time with AFM like it is with a micro-scratch tester or with our simulations, due to the characteristics of the technique itself.

6. Conclusions

This work has employed computer simulations to study the scratching behavior of an HDPE computer model with classical MD. Although these simulations have focused on a model defined to simulate HDPE, other polymeric materials could be simulated in the same fashion. This capability has been used to obtain the typical tribological properties assessed in materials.

From the results we can clearly observe that an increasing force results in increasing R_p and slightly decreased φ . Also, a larger indenter (while maintaining the total scratching force constant) results in a smaller R_p . After scratching, the material does recover partially in a significant and quick manner, like a viscoelastic material should under elastic strain.

Simulating the scratching behavior of polymeric materials can provide information on recovery rate and effects of chain spatial arrangement. Moreover, it can help us better understand the specific mechanisms responsible for the tribological properties of these materials. The simulations provide much more information than experimental testing alone, and should be used synergically with experimental results. Fig. 2 showing behavior of individual statistical polymeric segments as a function of time during a scratching test is a good illustration of this situation.

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