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Molecular dynamics computer simulation of scratch resistance testing of polymers: Visualization

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Abstract Experimental scratch resistance testing provides two numbers: the penetration depth R_p and the healing depth R_h. In molecular dynamics computer simulations we create a material consisting of N statistical chain segments by polymerization; a reinforcing phase can be included. Then we simulate movement of an indenter and response of the segments during X time steps. Each segment at each time step has three Cartesian coordinates of position and three of momentum. We describe methods of visualization of results based on a record of 6NX coordinates. We obtain a continuous dependence on time t of positions of each of the segments on the path of the indenter. Scratch resistance at a given location can be connected to spatial structures of individual polymeric chains.

Keywords: Molecular dynamics simulation; Scratch resistance; Polymer tribology

Introduction

The usage of polymer based materials (PBMs, polymers and polymer containing composites) grows at a fast rate. Most literature on PBMs deals with their mechanical

properties, thermophysical properties or else with processing and rheology. There is much less literature on tribology of PBMs: their scratch resistance, wear and friction – important in a number of applications such as coatings in electronics.

The term tribology has been coined in 1966, in a British governmental report of a committee headed by H. Peter Jost [1, 2]. In 1965 appeared an important book by Ernest Rabinowicz [3] which has its second edition 30 years later [4]. In 1978 appears a book by Horst Czichos [5] who advocates a systems approach to tribology. Rabinowicz [4] says: "The Jost Report actually greatly underestimates the financial importance of tribology. The Report paid little attention to wear, which happens to be (from the economical point of view) the most significant tribological phenomenon". For metals and polymers we can mitigate scratching and wear and lower friction by application of external lubricants, mostly liquid ones. Applying them to PBMs, we find that often swelling of the material takes place [6, 7]; the lubricant makes only the situation worse - so that other approaches have to be developed.

Computer simulations including Monte Carlo and molecular dynamics (MD) methods can provide a wealth of information and explain mechanisms of behavior inaccessible experimentally [8 - 14]. The situation described above behooves us to acquire *understanding of mechanisms of scratching* PBM surfaces. The key problem is obtaining pertinent information from a huge amount of results of each simulation run.

Molecular dynamics simulations of PBMs

We use the concept of statistical chain segments so that each particle in our simulations represents a number of real chain polymeric segments [15]. We shall deal with the creation of a material in the next section. MD simulations procedure has been described before; see for instance [9]. At the beginning of each time step updated velocities are calculated for each particle, in our situation as a function of the total force F acting on a given particle. F consists of forces created by intramolecular and intermolecular interactions, plus the external applied force. The new velocities are then scaled to maintain a constant temperature.

Simulations have been performed using the molecular dynamics method, initially developed by Alder and Wainwright [16] at the Lawrence Livermore Laboratory. Segments interact according to a set of pre-defined so called Lennard-Jones potentials [17] (originally defined by Gustav Mie [18]), which are defined as a function of the intersegmental distance. A detailed

description of the simulation model has been provided before [19]. The employed simulation parameters and interaction potentials have been discussed earlier [20].

The problem is the amount of information resulting from each MD simulation run. The material consists of N statistical chain segments. To simulate experimental scratch resistance determination, we provide time for equilibration and then simulate movement of an indenter applying force F on the surface and recording the response of the segments – for a total of X time steps. Each segment at each time step has three Cartesian coordinates of position and three of momentum along the Cartesian axes. The result is a record of 6NX stored coordinates. We describe in this paper procedures of extracting meaningful information from such a record.

Creation of a polymer

Creation of a polymeric material on a computer has been also described before [9]. One starts on a lattice of particles, performs polymerization, and then performs equilibration of the material in function of the interaction potentials, internal inside the chains and external ones. The result is an off-lattice material, with a certain amount of free volume introduced during polymerization. We first need to see the material. Composites and nanocomposites of the type polymer + reinforcement are growing in importance [21 – 29]. Therefore, we need the capability to place reinforcement at specific locations throughout the polymeric matrix. Simple shapes of reinforcing particles include spherical or cylindrical (fibers, carbon nanotubes). Placing small spherical particles is relatively easy. In Figure 1 we show a more complicated case: a PBM consisting of a polymeric matrix plus cylindrical reinforcement placed at specific locations with respect to the material surface.

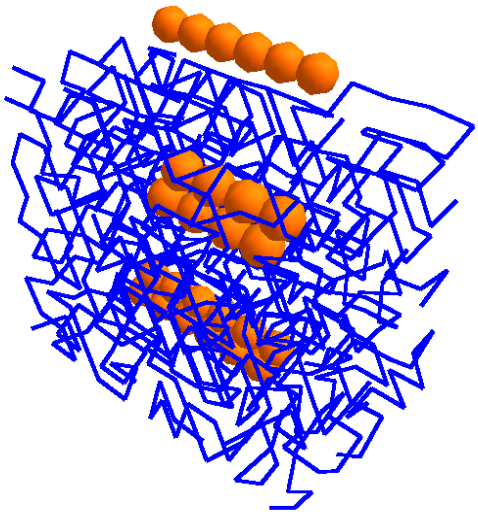

Figure 1. A polymer with a cylindrical reinforcement at various levels with respect to the surface.

There is virtually an infinity of spatial structures of chains. We need to be able to track the chains individually – at least those which have one or more segments in the path of the indenter. Therefore, we provide different colors to the chains; see Figure 2 for a neat polymer.

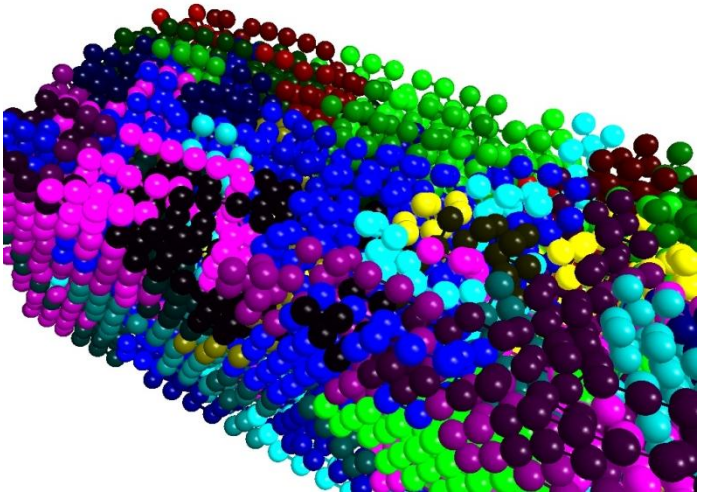

Figure 2. A neat polymer with each chain marked by a different color.

The amount of information in Figure 2 is already large. We have the capability to focus on, say, two chains and see how at the local level they have responded to the deformation caused by the indenter; see Figure 3. Note that Figure 3 is in a 3D perspective, thus objects further away from the viewer look smaller.

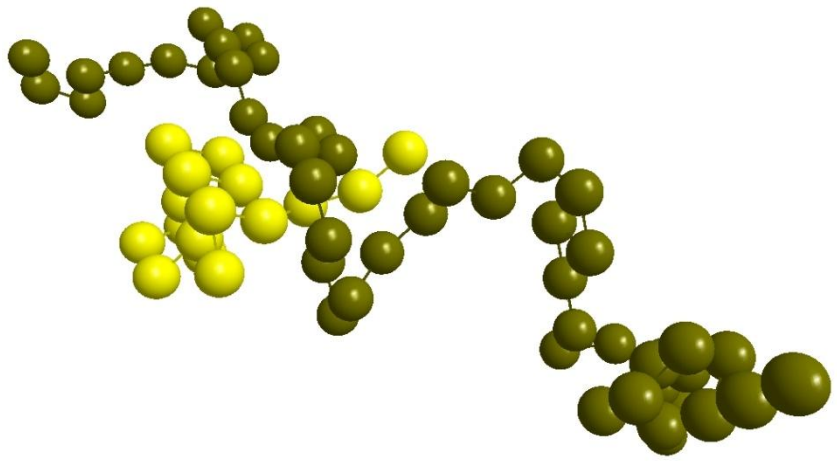

Figure 3. Two chains only

Simulation of scratching

The scratching program we have created allows application of indenters of various size and shape. This is illustrated in Figure 4. Segments are illustrated by spheres, those on which the the indenter is actually exercising a force at a given time are marked red.

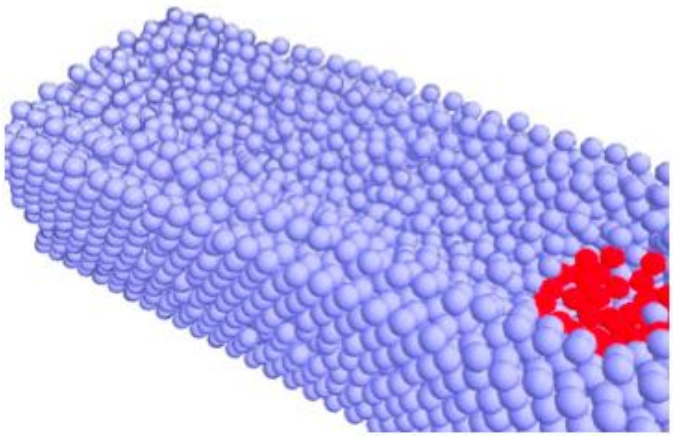

Figure 4. View from the top for an indenter moving from left to right. The size and actual location of the indenter are marked by red segments. We see the groove already formed behind the track of the indenter.

Both round and square indenters have been used in simulations thus far; actually, any shape could be defined for the indenter geometry. The indenter sizes currently considered range from a diameter of two to seven statistical segments. On the one hand, we want to ensure that, at the lower end, the indenter always acts on several segments simultaneously. On the other hand, we defined that the indenter diameter should not extend more than half the width of the material – so as to prevent edge effects.

Anlysis of simulation results

Again there is a problem of extracting pertinent information – such that could be connected among others to the spatial distribution of the chains as exemplified in Figure 2. Experimental scratch resistance testing of polymers provides two numbers: the instantaneous or penetration depth R_p and the recovery or healing depth R_h. We need to relate these numbers to MD results.

As previously stated, we obtain from the simulations 6NX coordinates. While the simulation is running, it is impossible to predict exactly which segments will be scratched subsequently;

this depends on how the entire surface responds to the scratching thus far. Therefore, calculations and visualizations have to be done after the simulation has terminated. The individual data files for each time step are also used by a 3D visualization application, using OpenGL rendering [30]; see again Figure 4. This application enables the user to freely pan and rotate the material in 3D, and to animate its behavior along time. OpenGL is a low-level graphics library specification. As OpenGL is not a programming language but a library, it can be called from applications written in any of the major high-level programming languages. It makes available to the programmer a small set of geometric primitives such as points, lines, polygons, images, and bitmaps, which can be rendered in a virtual 3D space and then visualized from any desired perspective. OpenGL provides a set of commands that allow the specification of geometric objects in two or three dimensions, using the provided information along with commands that control how these objects are presented.

In the present work, the authors have coded their graphical application in Microsoft Visual C++ under a Windows 32-bit framework, and employed the OpenGL library to render each of the material's elements (statistical segments, bonds, nanoparticles, and nanofibers).

The indenter hits several segments on the surface simultaneously; it is the combined response of those segments which is pertinent. The simulation progress is recorded periodically to status files, together with information on which segments were being scratched at that moment. After the simulation is completed, an application reads all these files, establishes the precise motion of the indenter along time and the respective scratched segments, and searches all the results files for the vertical position of each pertinent group of scratched segments. That information is then exported to a simple character delimited text file. A spreadsheet application can then open these files and produce plots such as that in Figure 5. The diameter of the indenter is here comparable to the size of three segments.

We see in Figure 5 that shortly after being 'attacked' by the indenter each segments reaches a certain maximum depth. The average of these depths provides the penetration depth R_p seen also in experiments. Since all polymers are viscoelastic, a recovery takes place – as it does in experiments. We see that each segment reaches a certain horizontal plateau – typically below its original position at the surface. The average of these plateaus is the residual or healing depth R_h. In experiments one has defined the viscoelastic recovery f [31] as

$$f = [(R_p - R_h) \cdot 100\%]/R_p \qquad (1)$$

One can also consider the brittleness B [32, 33]

$$B = 1/(E'_{b}) \quad (2)$$

where E' is the storage modulus determined at 1.0 Hz by dynamic mechanical analysis [34] while $_{b}$ is the elongation at break in tensile testing. There is a relationship between f and B valid for a large variety of polymers and composites, namely [32, 33]

$$f = 30.6 + 67.1e^{-B/0.505} \quad (3)$$

To compare simulation results with experimental ones, we need to compare pairwise the values of R_p, R_h and the resulting viscoelastic recoveries f.

As said above, experiments provide only two numbers. Figure 5 provides orders of magnitude more information. We acquire the local response at each position along the scratching path, and also the final surface profile after full recovery of the material.

It is this type of information that gives us an opportunity to understand scratching mechanisms and scratch resistance of polymers and PBMs. Local responses at a given location can thus be related to the spatial structure of the chains such as shown in Figure 1b. For the future we consider application of focused ion beam milling [35] to PBM surfaces. We should be able to simulate milling as well as indentation (also application of an indenter, but this time a stationary rather than a moving one) by molecular dynamics.

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