Tribology of Polymers and Polymer-based Materials

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A development in industry: In several areas gradual replacement of metallic components by polymer-based materials (PBMs). Reasons:
* PBMs are dramatically more benign to the environment
* have low density (car or plane mileage/gallon higher than for metals)
* better ability to absorb shocks and vibrations
* operate with little power and low noise
* can have optical transparency
* show good adhesion to many substrates
* require very low maintenance

Problems:
* much weaker mechanically
* high scratchability (as Teflon coating on a frying pan)
* properties change with time, long term prediction from short term tests necessary
* high wear; consider now this single issue more in detail

IMPORTANCE of TRIBOLOGY

Key Areas of Tribology:

- **Friction**
- **Scratch Resistance**
- **Wear (consequence of Abrasion)**
- **Design of Interacting Surfaces in Relative Motion**

ERNEST RABINOWICZ of MIT in Friction and Wear of Materials, 2nd edn., Wiley, New York 1995:

"In the late 1960s the British government was persuaded by the Jost Report (1966) that much waste of resources (estimated to be 515 million pounds sterling per year) occurred because of ignorance of mechanical surface interaction phenomena, and a coherent program of education and research was launched to remedy this situation. The word 'tribology' was coined to describe this program and the use of this term has become widespread. 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."

Reasons why tribology is needed:

Two problems causing expenditures of billions of dollars by industry each year are **wear** and **corrosion**. Because of these problems, components and sometimes entire structures have to be replaced periodically. It is among others to avoid corrosion that we have the ongoing process of replacements of bulk metal components by polymeric ones in aviation, automotive and other industries. Metallic and ceramic materials provided with coatings also achieve similar purposes including corrosion protection.

Reasons why tribology of polymer-based materials (PBMs) is difficult:

Polymeric components and coatings wear and scratch easily (Teflon). Wear in metals and ceramics can be mitigated by external lubricants. However, in polymers external lubricants often cause swelling, although rare exceptions exist. Also liquid lubricants are mostly not desired in high velocity devices such as polysilicon micromachines (MEMS) which require shearing the fluid surrounding the machine -what leads to damping. Thus, the ongoing miniaturization in electronics and -related industries requires development of new strategies in polymer tribology. In -spite of its tremendous importance, tribological processes in polymers are still insufficiently understood. The understanding is needed to create PBMs with high scratch resistance, low wear, and in certain cases low friction.

In the following we shall discuss the basics of tribology and some examples how problems in tribology can be solved.

Fundamentals of Tribology

The science of *Tribology* (Greek *tribos*: *rubbing*) concentrates on contact mechanics of moving interfaces that generally involve *energy dissipation*.

Adhesion is a term relating to the force required to separate two bodies in contact with each other.

Friction can be defined as the tangential force of resistance to a relative motion of two contacting surfaces:

$$F = \mu \cdot N \qquad (1)$$

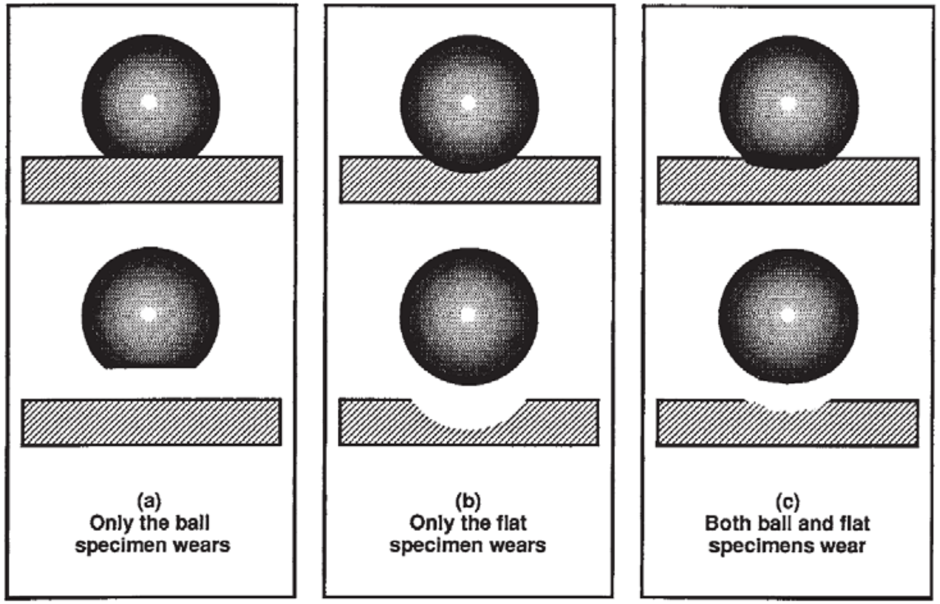
where N represents the normal force and μ represents friction. One works here with two values. In a stationary specimen we have the static friction, namely the force required to create motion divided by the force pressing mating surfaces together. This quantity is often called the static “coefficient of friction”, although - as pointed out long ago by Lord Kelvin -the word “coefficient” conveys *no information*. For a specimen in -motion we have the dynamic friction (also called *kinematic friction)*, - that is the force required to sustain motion at a specified surface velocity - divided by the force pressing mating surfaces together. Similarly here, -the term dynamic coefficient of friction is still used.

The first laws of tribology were formulated already in 1699 by Amontons [1]:

1) The resistance caused by friction is proportional to the load.
2) That resistance is independent of the apparent area of contact.

Eq. (1) above agrees with the First Law of Amontons. Both laws are useful, although modern data show that the laws are not obeyed exactly.

To consider **wear**, let us first look at some simple cases:



The classical definition of wear is based on the formula

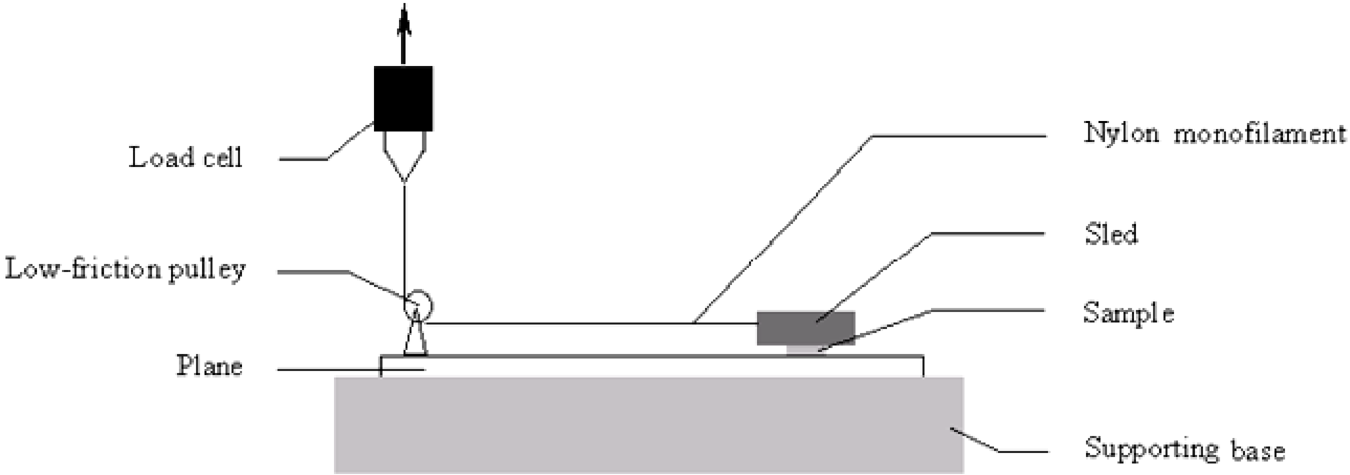
$$u_{sp} = V_{loss}/(F.D) \qquad (2)$$

where u_{sp} = wear rate; V_{loss} = the loss in volume of the sample; F = applied force; and D = sliding distance. This definition does not take into accounts various factors which affect V_{loss}. A simple method of determination of wear using Eq. (2) involves abrasion, such as with the Tabor abrasion tester.

We shall now present recent experimental methods of determination of tribological properties along with some examples of results.

Determination of static and dynamic friction

The testing machine should permit the use of a moving sled - on which the parallelepiped sample is attached - with a stationary plane:



The ASTM D-1894 standard allows also the opposite option, that is the use of a stationary sled with a moving plane. The standard recommends the speed of 150 mm/minute, the temperature of 23°C ± 2°C and 50 % ± 2 % relative humidity. In practice we use lower speeds to achieve higher accuracy - what is particularly important in small specimens to be tested.

Static and dynamic friction can be conveniently determined by installing a friction attachment to a universal mechanical testing machine. A load cell is then used to measure the force needed to slide the sample over the plane.

Static and dynamic friction values

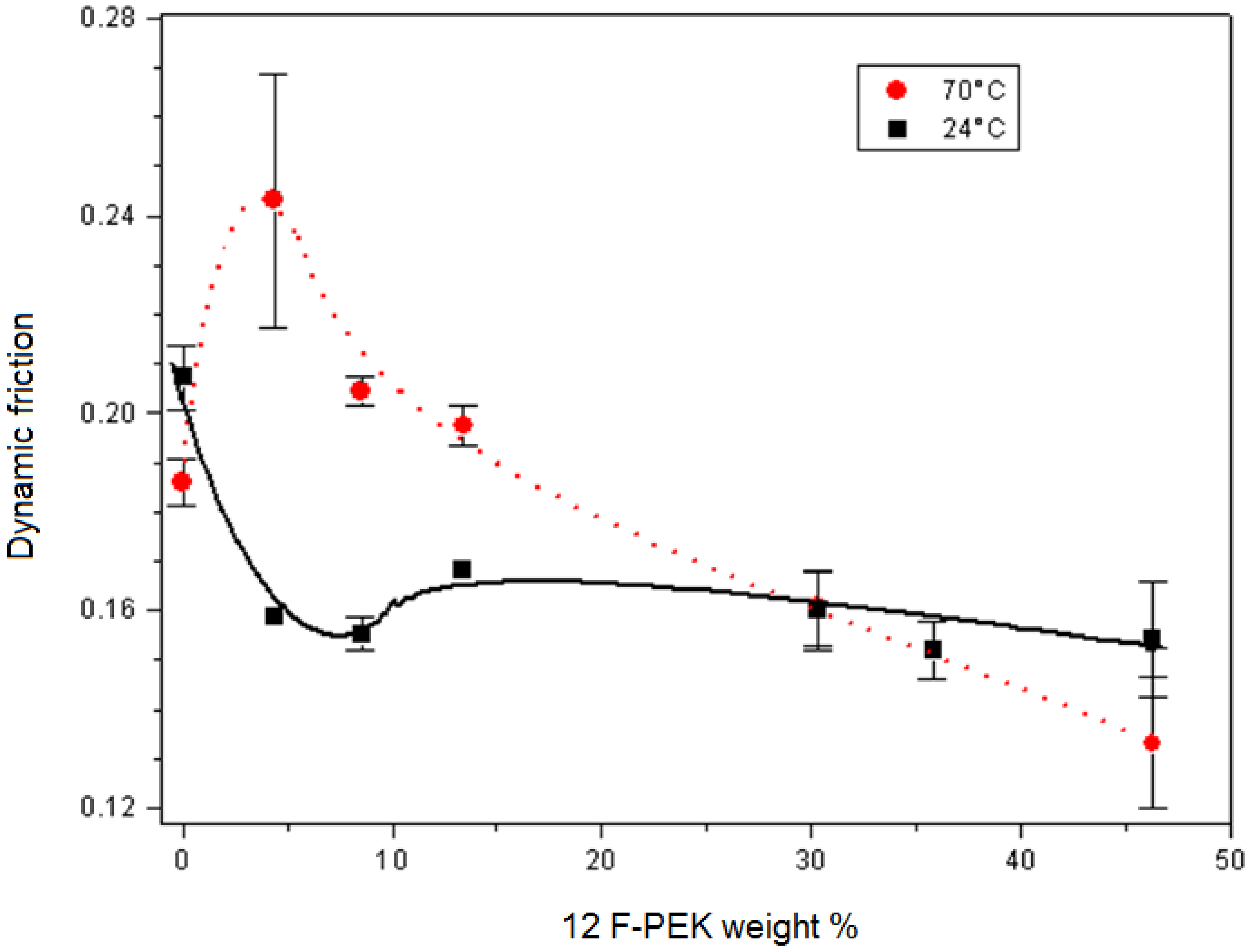
	static	dynamic
cast iron on cast iron	1.1	0.15
steel on steel (unlubricated)	0.7	0.6
copper on steel	0.53	0.36
wood on wood	0.4	0.2
glass on glass	0.94	0.40
ice on ice	0.1	0.03
rubber on dry concrete	1.0	0.8
rubber on wet concrete	0.7	0.5
Teflon on Teflon	0.04	0.04
Teflon on steel	0.04	0.04
polyethylene on steel	0.15 – 0.20	0.10 – 0.14
polystyrene on polystyrene	0.5	0.5
waxed ski on snow	0.14	0.05
Synovial joints in human limbs	0.01	0.01

An example of tribology improvement:
a commercial epoxy + a thermoplastic additive

The problem here was the usual one: reinforcing the epoxy so as to improve its tribological properties. We were interested in both lowering friction and increasing scratch resistance. Comments from tribologists were *not* encouraging. We were told one can one of these properties or the other, but not both at the same time. Teflon was used as an example that low friction excludes high scratch resistance.

Epoxies are thermosets, with a very wide range of applications. The rate of curing (crosslinking) is important; see B. Bilyeu, W. Brostow and K.P. Menard, J. Mater. Ed. 2001, 23, 189.
We have decided to perform curing at the room temperature and also at 70ºC. We have chosen to use a thermoplastic fluoropolymer (F-PEK, FP) as the additive to modify the tribology of the epoxy.

We have determined first static and dynamic friction, and then in scratching tests the penetration (instantaneous) and recovery (final) depths



Results for static friction are similar

At least three questions arise from the previous diagram:

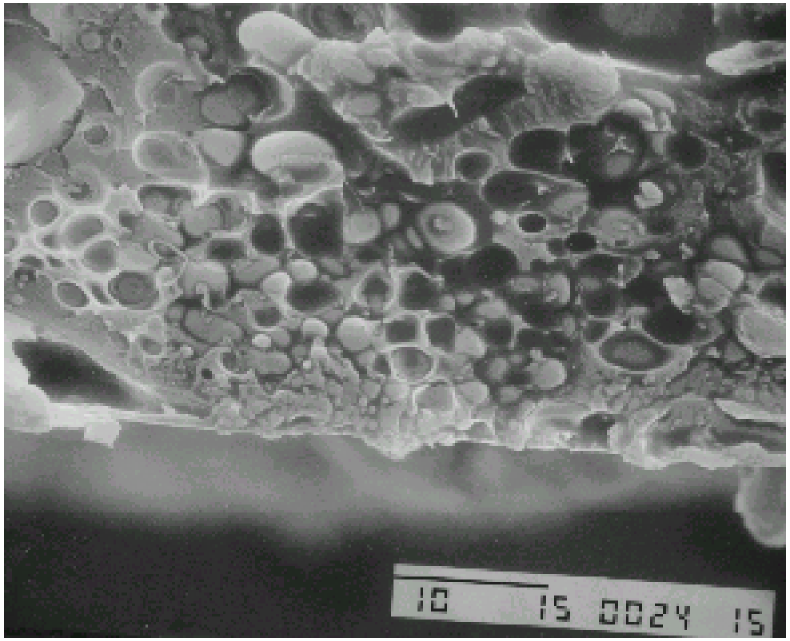
- How does it happen that curing at 70°C causes an **increase** of dynamic friction while curing at 24°C causes a **decrease** ?

- How does it happen that addition of only 5 weight % of the fluoropolymer additive causes such dramatic changes - in both directions - of dynamic friction ?

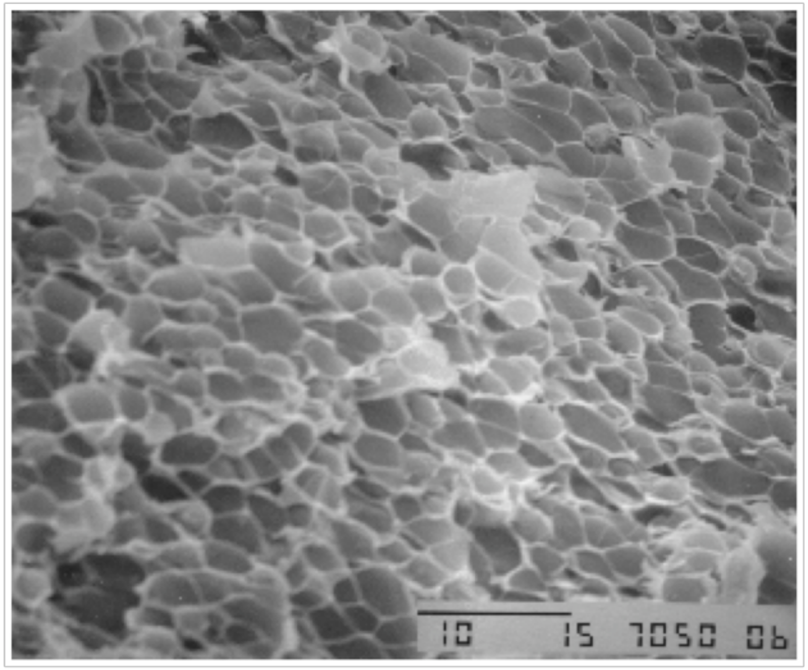
- Why do we have extrema followed by relatively flat plateau-like curves ?

To answer these questions we need to look at surfaces under a scanning electron microscope (SEM)

Surfaces under the SEM



SEM of 15 % fluoropolymer blend cured at 24^{o}C



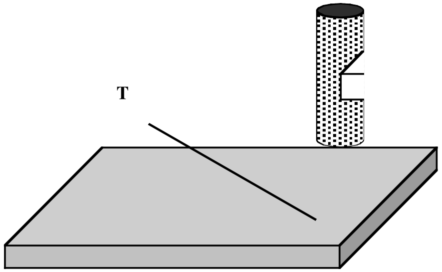
SEM of 30 % fluoropolymer blend cured at 24^{o}C

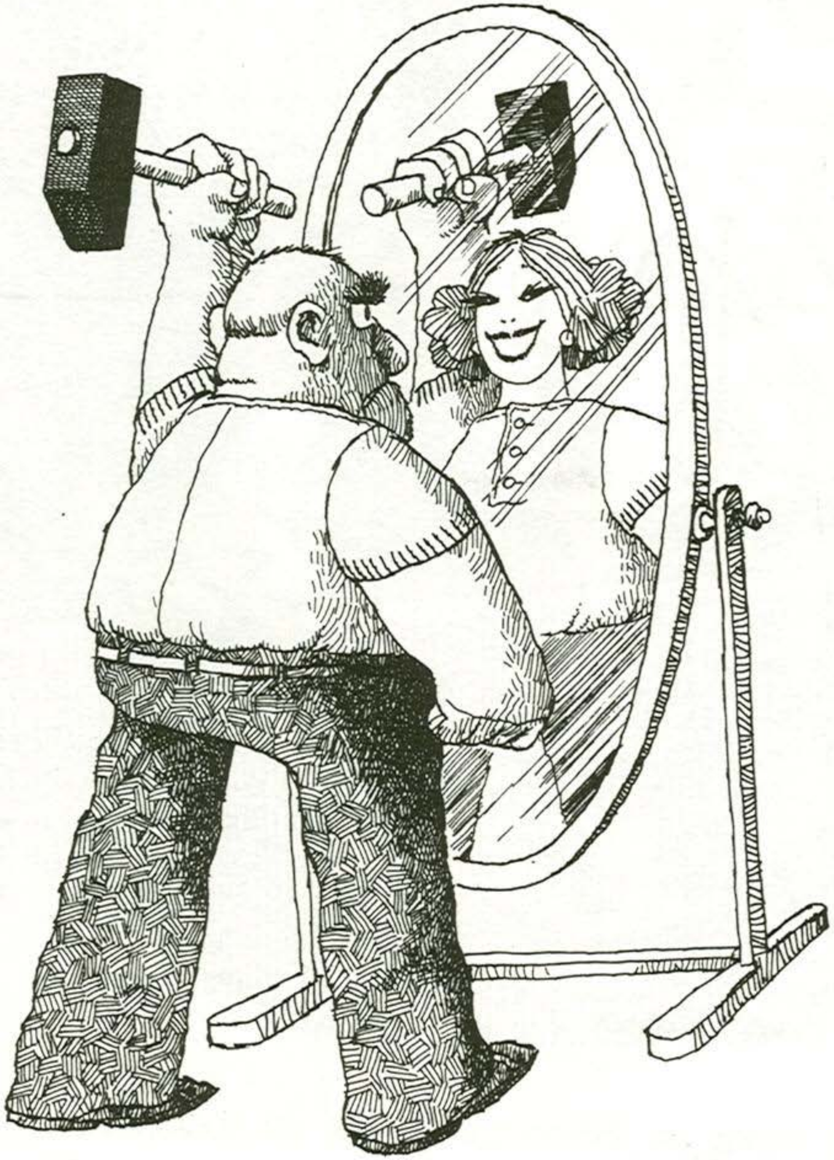
Conclusion: fluoropolymer which is the minority component arrives preferentially at the surface (it has *low surface tension*) and tries to become the **majority** phase which forms the matrix

MICROSCRATCH TESTER

determines

- surface topography
- penetration depth
- residual depth
- tangential frictional force
- acoustic response of the material





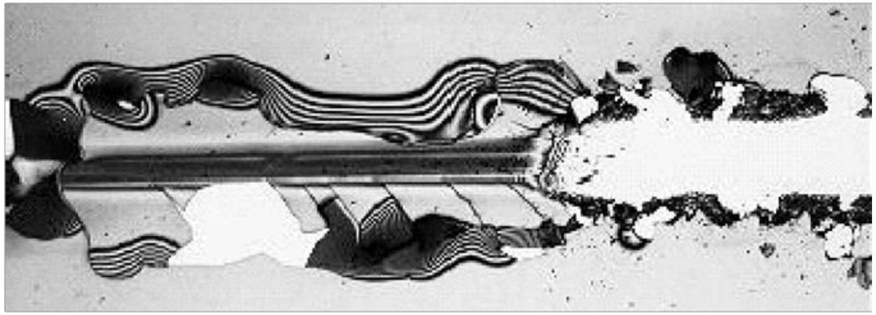
As in the Quino cartoon, an action causes a reaction.

Materials **resist** any attack from outside. Thus, a bent material sample tries to unbend.

A polymeric sample scratched by an indenter undergoes healing.

Determination of scratch resistance

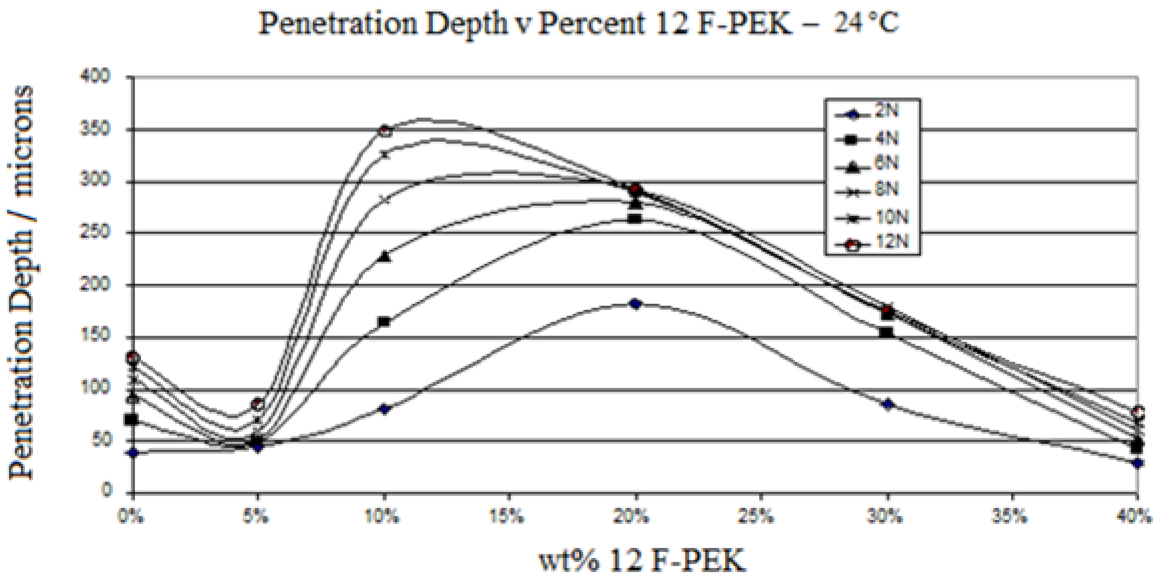
One determines the instantaneous penetration depth R_p. After viscoelastic recovery (healing) which usually takes 3 minutes (the second experiment is performed after 5 minutes) one measures the recovery depth R_h. The accuracy of the determination is ± 7.5 nm



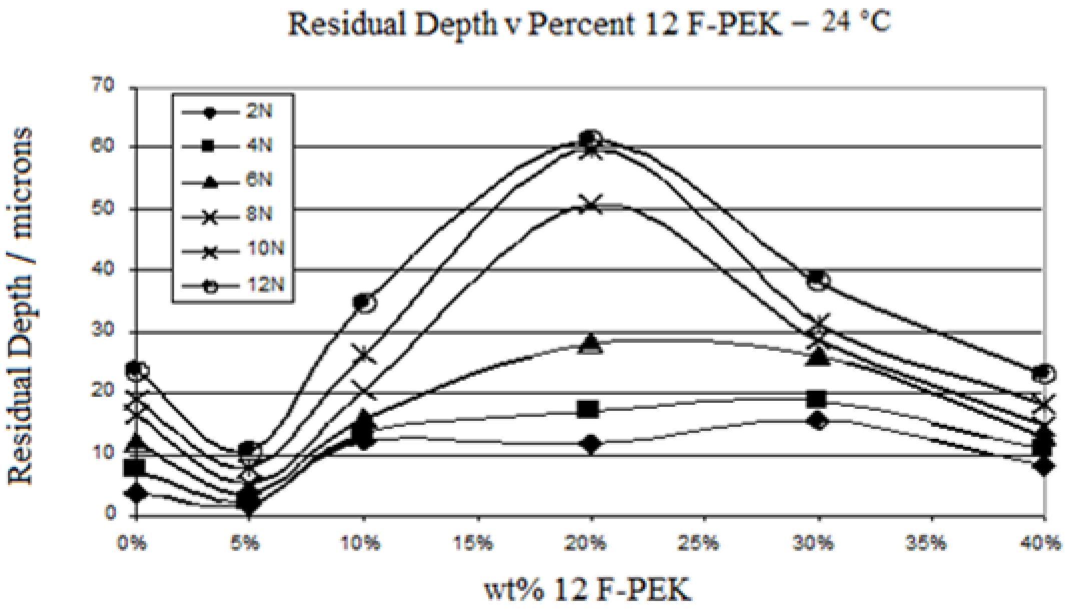
An enlargement of the scratching path (groove) after the test in microscratch tester

Testing is performed under under a constant or else under a progressively increasing force or else under a stepwise force

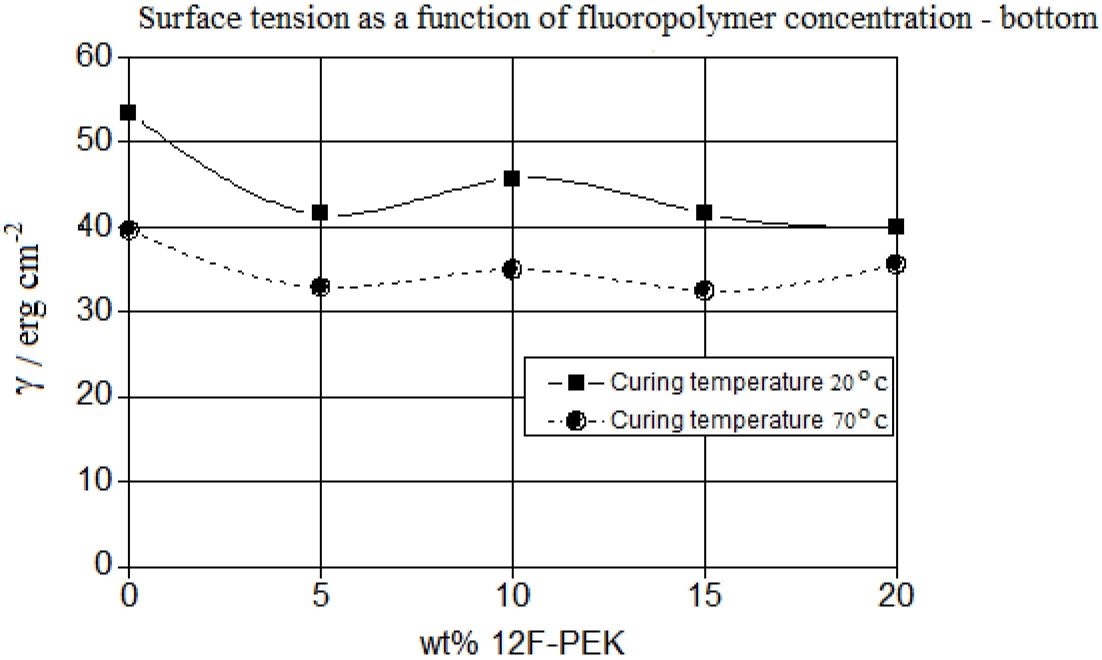
Multiple scratching along the same groove is possible, providing sliding wear results

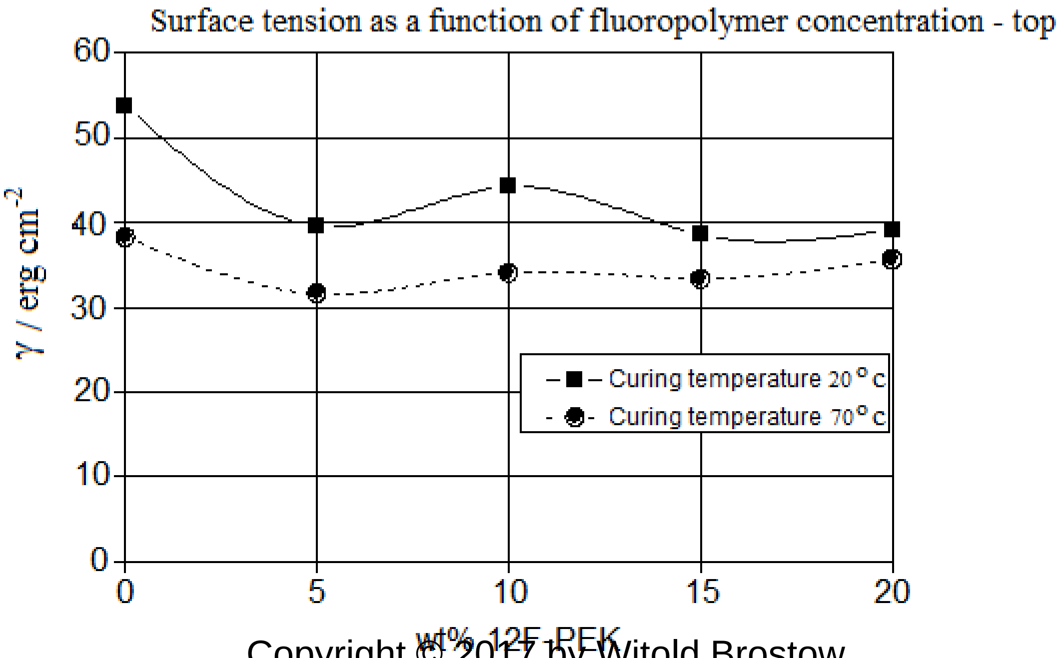


Penetration Depth v Percent 12 F-PEK – 24 °C



Residual Depth v Percent 12 F-PEK – 24 °C


Surface tension as a function of fluoropolymer concentration - bottom
γ / erg cm^{-2}
60
50
40
30
20
10
0
0
5
10
15
20
wt% 12F-PEK
Curing temperature 20 °c
Curing temperature 70 °c


Surface tension as a function of fluoropolymer concentration - top
γ / erg cm^{-2}
60
50
40
30
20
10
0
0
5
10
15
20
wt% 12F-PEK
Curing temperature 20 °c
Curing temperature 70 °c

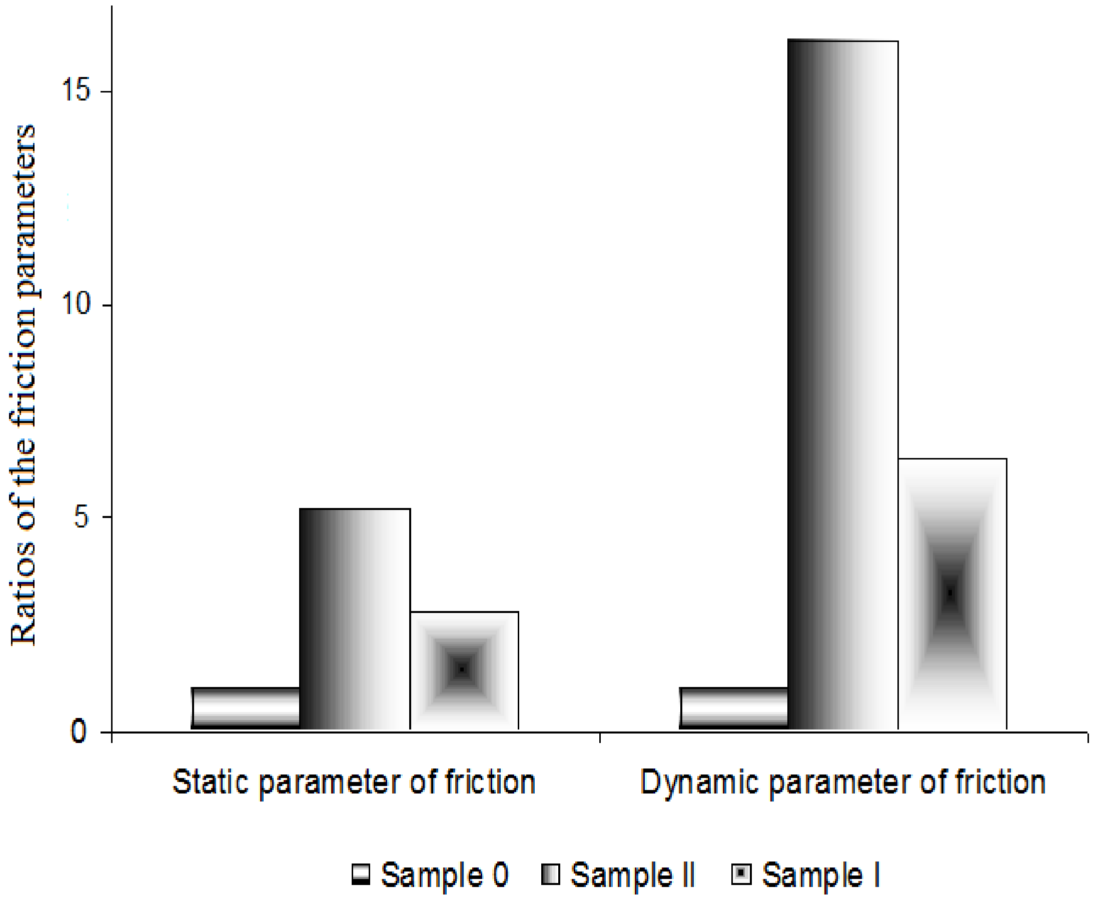
Conclusions from the epoxy + F-PEK system:

- it is possible to achieve simultaneously low friction (both static and dynamic), and high scratch resistance. At the concentration of 5 wt. % of the fluoropolymer, with curing at 24°C, we have both lowering of friction and lower scratch depth. The latter statement applies to both the penetration depth (= instantaneous depth when the indenter has "attacked" the surface) and the recovery depth (= the final depth after healing has taken place).
- curing temperature is very important. When we cure at 70°C instead of at 24°C, we get higher friction instead of lower.
- at the same concentration of 5 % FP we have also a minimum of surface tension. Thus, surface tension is of interest to tribologists. In fact, the reason why the fluoropolymer goes to the surface and produces the beneficial effects is its surface tension lower than that of the epoxy.

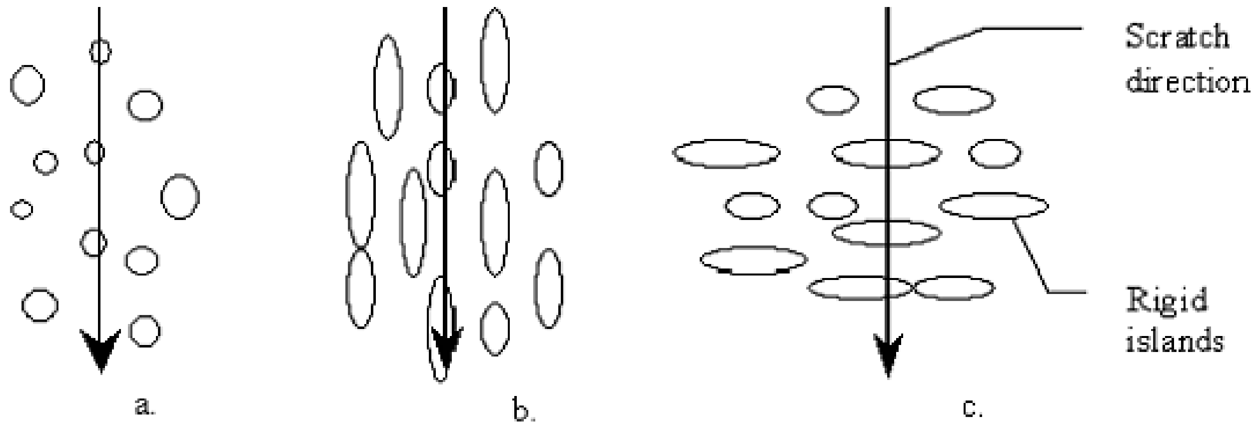
Magnetic field orientation

Polymers with dipole moments can be oriented in electric and magnetic fields. We have investigated the effects of such orientation on tribological properties of a polymer liquid crystal (PLC) PET/0.6PHB, where PET = poly(ethylene terephthalate), 0.6 is the mole fraction of the second (LC) component in the copolymer and PHB = p-hydroxybenzoic acid.

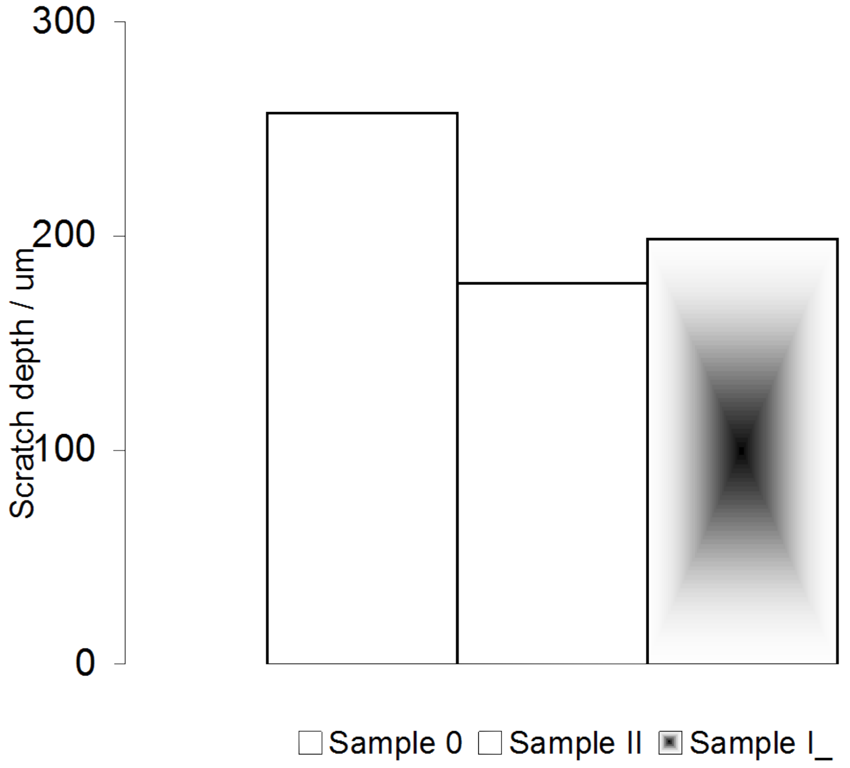
We have heated the PLC to 280^{o}C, applied the magnetic field of 1.8 Tesla, and maintained that field and that temperature for 30 minutes. Static and dynamic friction as well as penetration and recovery depths were then determined.



Friction determination results for the PLC. The friction is *higher* after the magnetic field was applied

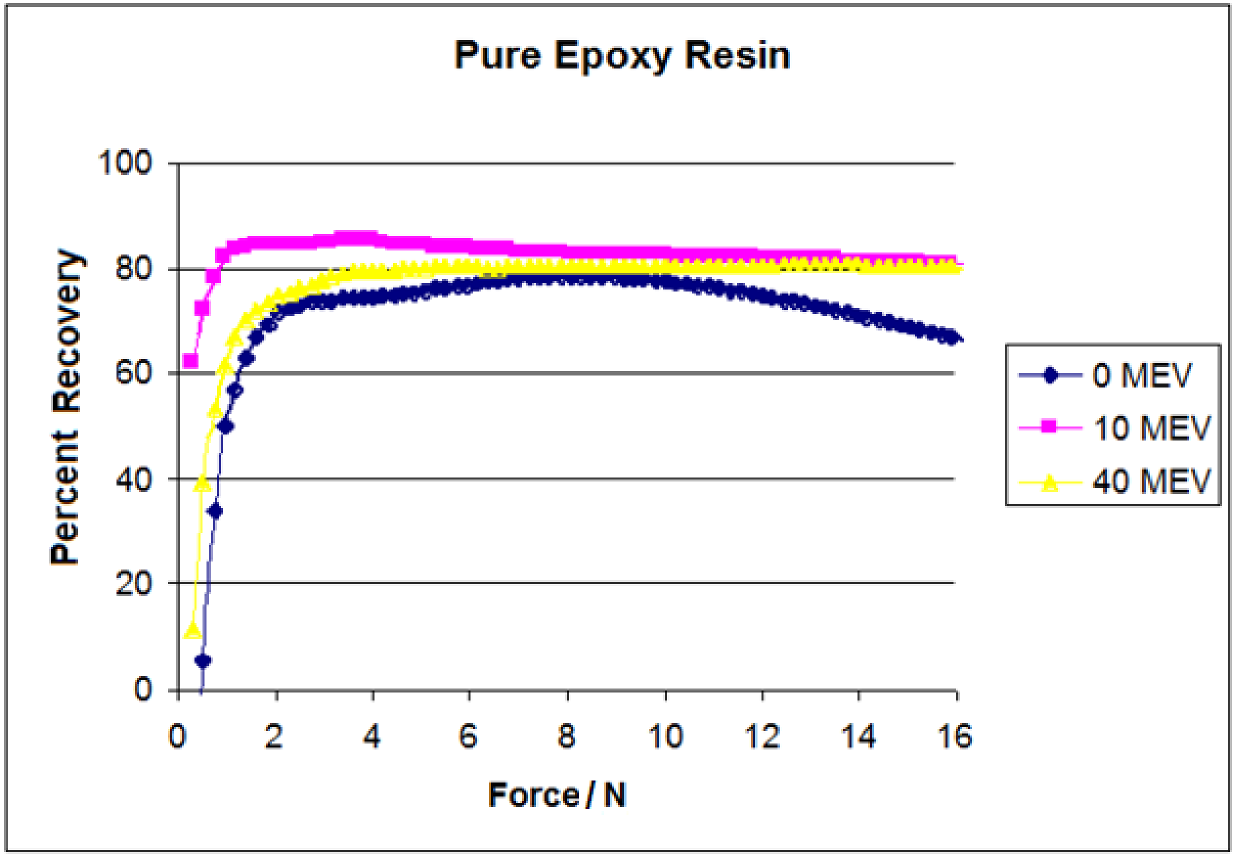


Explanation of the friction results for the PLC



Effects of magnetic field orientation on the penetration depth in scratch testing of the PLC. Here the field application does help, <u>shallower</u> scratch depth result

Irradiation with protons (in this case) and its effects on epoxy scratch resistance as percentage recovery

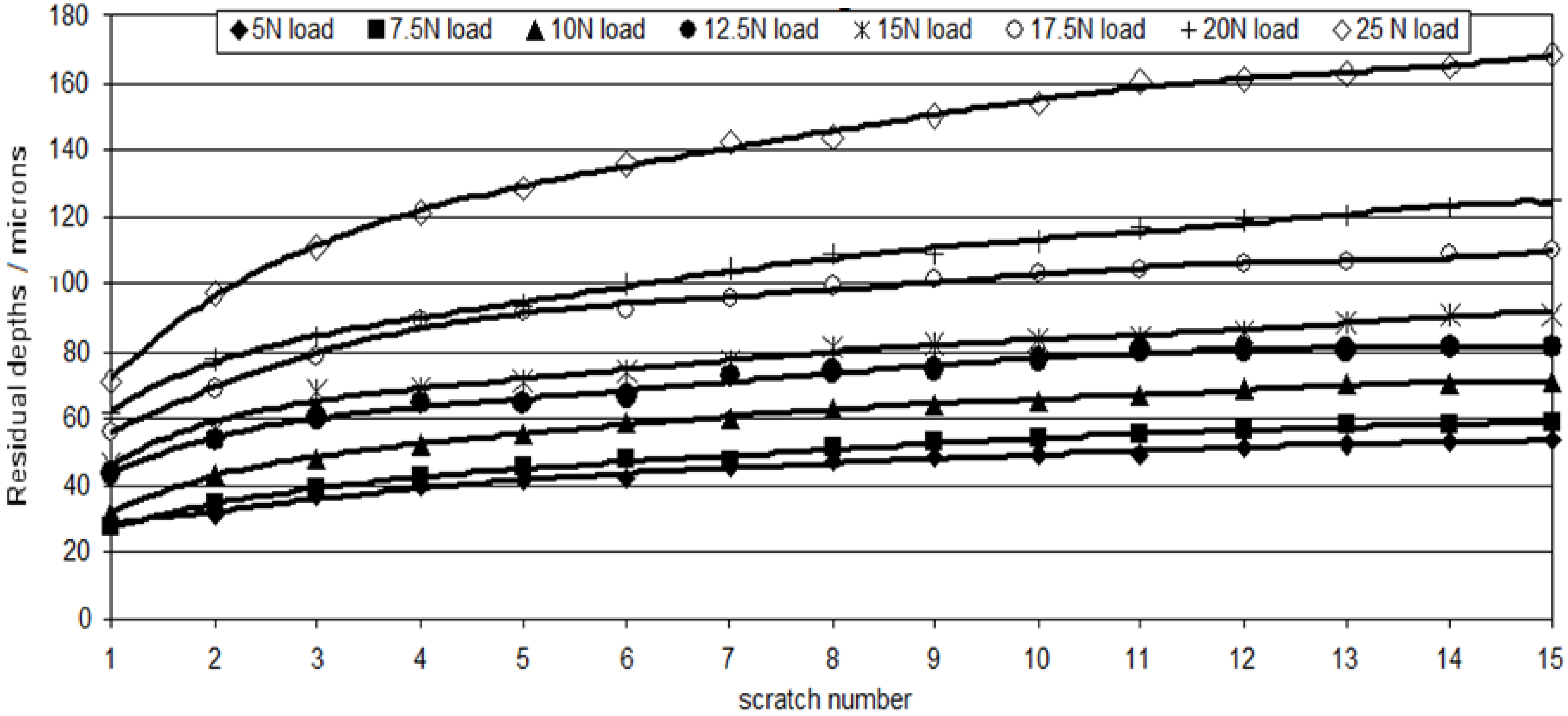


We see that, at diamond indenter forces of 10 N or more, irradiation at 40 MeV produces only slightly better results than at 10 MeV. In either case, irradiation helps

Sliding wear

Recall the micro scratch tester allows also another very useful option: multiple scratching along the same groove, resulting in the determination of the <u>sliding wear</u>. This is a more accurate method of wear determination than the abrasion wear. The results are not equivalent, however. In sliding wear one determines again two basic quantities, the penetration depth and the recovery depth, now as a function of the number of the scratching experiments.

Multiple scratching of LB-18 (a polyester)



This is an example of our discovery of strain hardening in sliding wear (an Intel prize to the student Juliet Howe who discovered this phenomenon). After a dozen or so scratch tests, the residual depth does not change anymore. The number of scratches needed to achieve the constant depth increases somewhat with increasing load. See W. Brostow, G. Damarla, J. Howe and D. Pietkiewicz, e-Polymers 2004, no. 025 (http://www.e-polymers.org). Not all - but many - polymeric materials show this behavior. Polystyrene (PS) does not - what lead us to a definition of brittleness, showing how different PS is from other polymers

A definition of wear based on sliding wear experiments:

FOR A GIVEN INDENTOR GEOMETRY, TEST VELOCITY, FORCE F and at 25°C (or at ANOTHER PREDEFINED TEMPERATURE) WEAR(F) is

$$W(F) = \lim_{n \mapsto \infty} R_h(F)$$

where R_h is the residual (healing) depth and n is the number of scratches along the same groove.

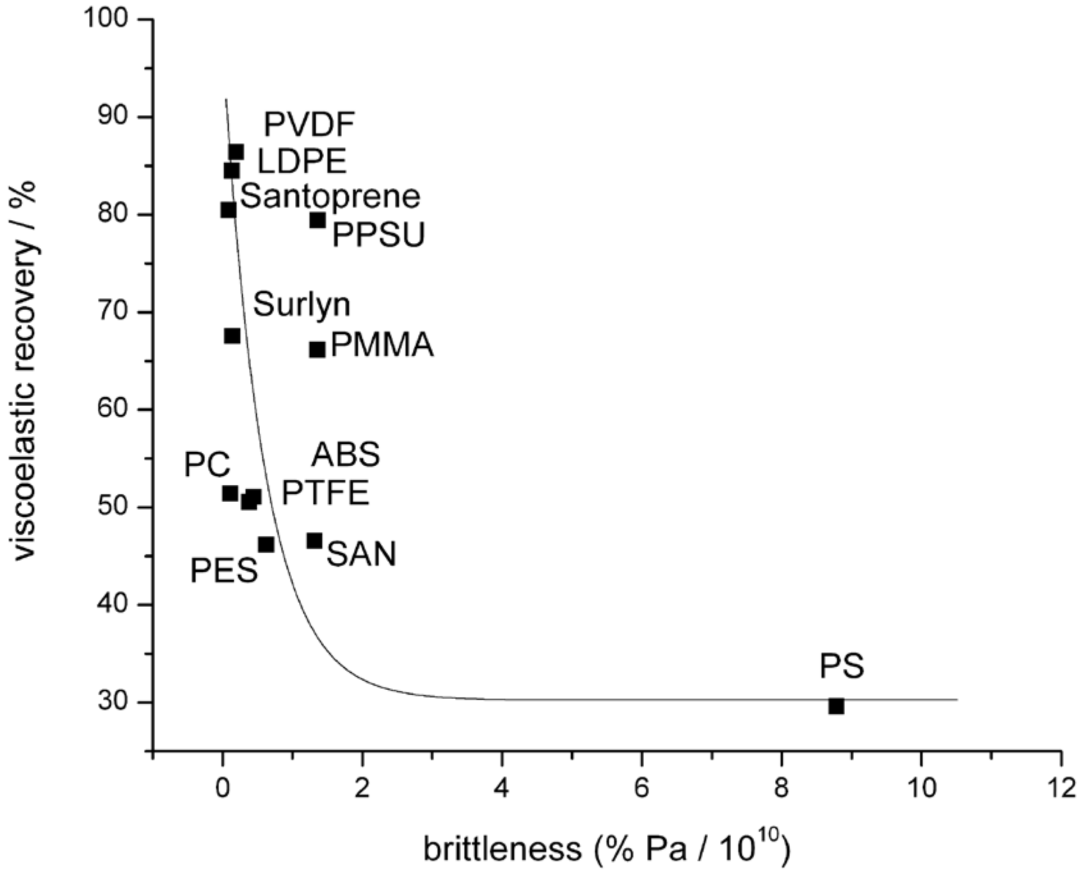
In practice one stops the experiments when

$$[R_h(n+1) - R_h(n)]/R_h(n) < 1\,\%$$

which typically occurs after 15 or so tests

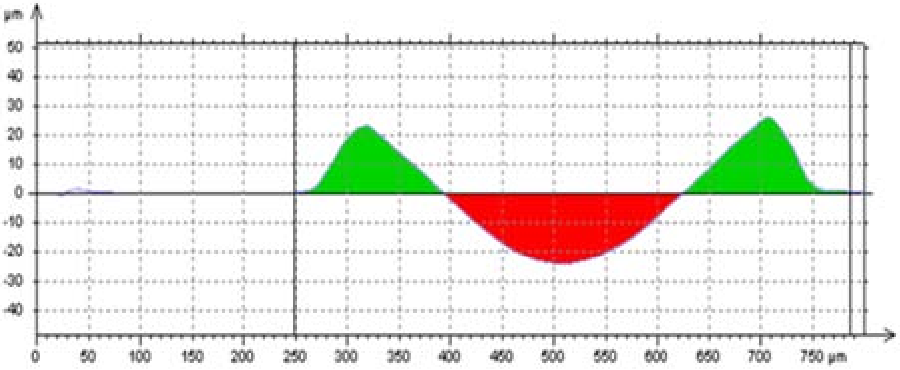
Important criterion: Brittleness defined as: $B = 1/(\varepsilon_b \cdot E')$

where ε_b = strain at break in tensile testing while E' = storage modulus in dynamic mechanical analysis (DMA)



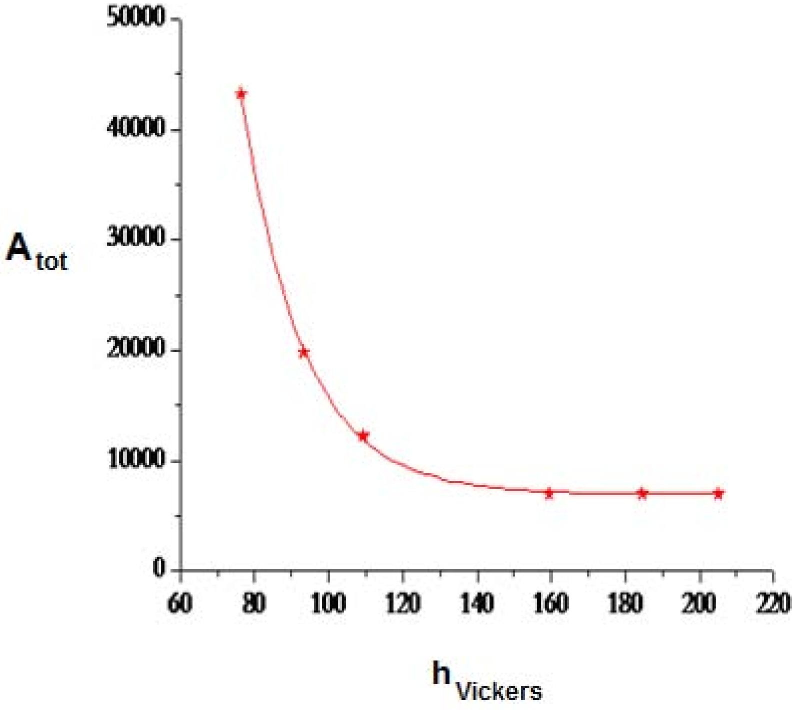
We have defined brittleness in 2006 since it was before a qualitative concept used in hand-waving discussions only. The Figure shows that B is related to healing or recovery in scratch and wear testing. Odd results of various kinds for polystyrene are now explained by its unusually high brittleness

Groove profiles in scratch testing related to hardness



Groove profile for polystyrene (PS) perpendicular to the indenter motion direction. Groove (inside) surface area = A_i (red) ; top ridge (outside) surface area = A_o (green) . Total surface area

$$A_{tot} = A_i + A_o$$

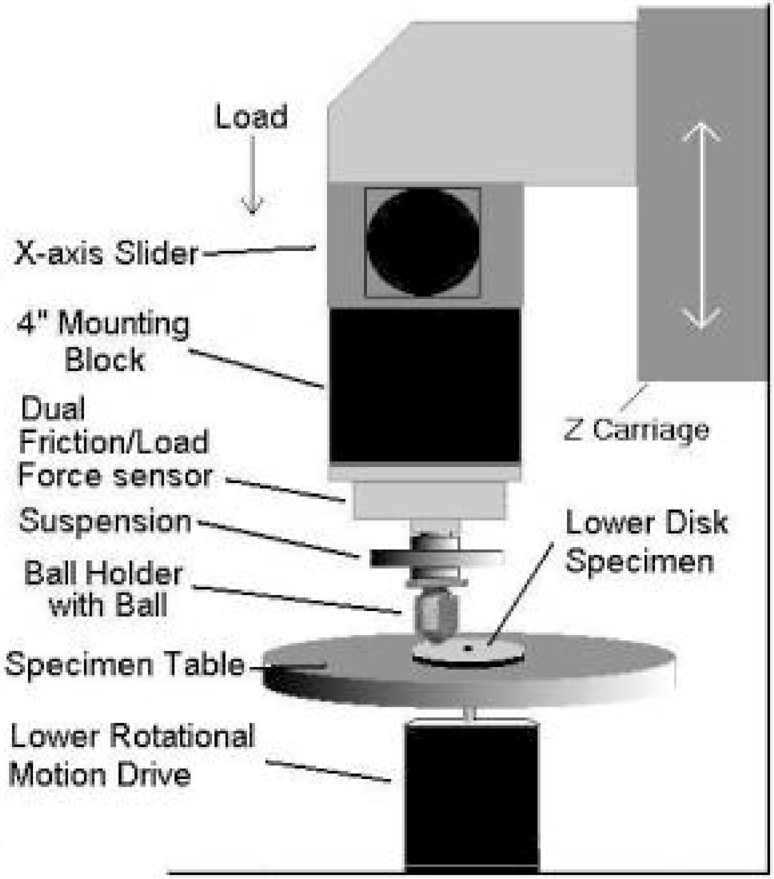


We have established a dependence between A_{tot} and theVickers hardness $h_{Vickers}$ for a variety of polymers with different structures and properties: PS, polypropylene (PP), polycarbonate (PC), polytetrafluoroethylene (PTFE, Teflon), low density polyethylene (LDPE), and polyethersulfone (PES):

$$A_{tot} = 6960 + 3.5 \cdot \exp(-0.06h_{Vickers})$$

The highest value of A_{tot} is for Teflon, the softest & easily scratchable material

Pin-on-disk tribometer for dynamic friction and wear



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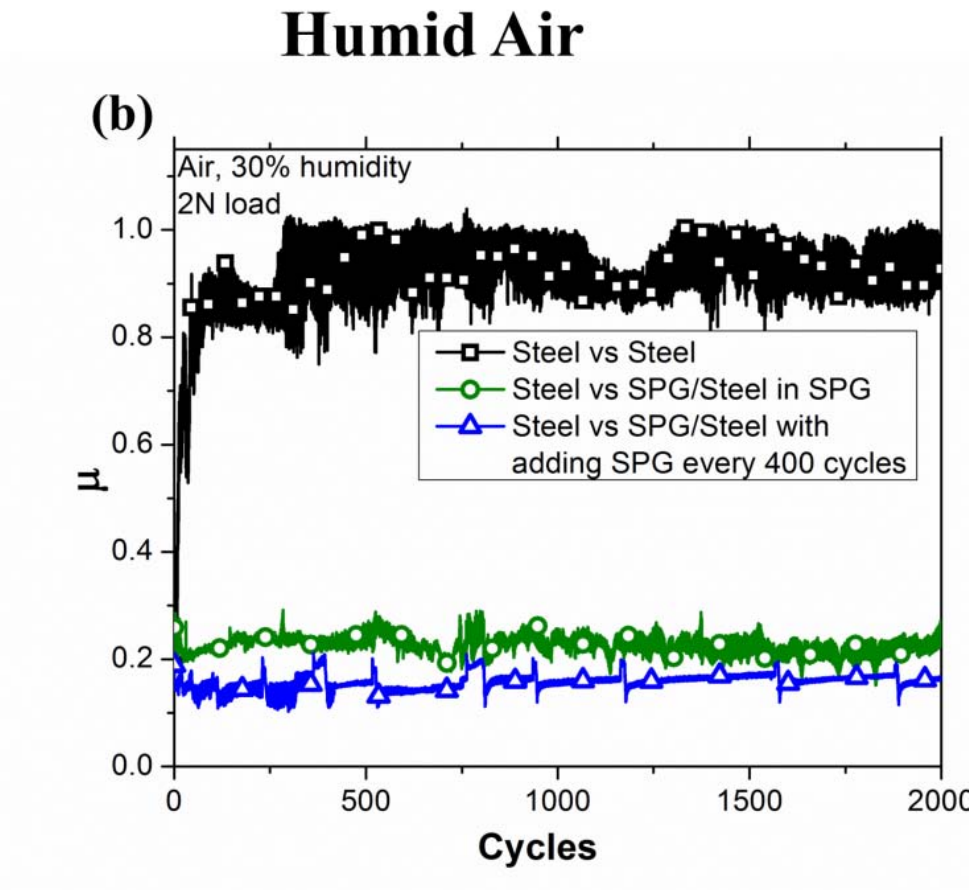
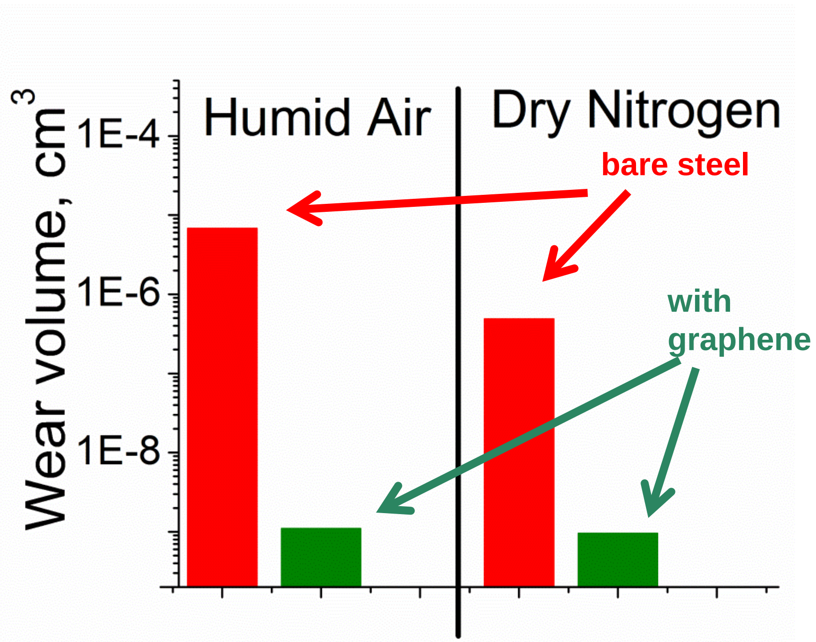
Dynamic friction of steel vs. steel:
Effect of solution-processed graphene (SPG)



Wear Rate of steel with and without graphene



Using additional solid lubricants for friction and wear reduction

REASONS FOR COMPUTER SIMULATIONS
in Materials Science and Engineering

CAPABILITY TO OBSERVE PHENOMENA AND PROCESSES INACCESSIBLE EXPERIMENTALLY - PARTICULARLY THOSE AT THE MOLECULAR LEVEL. Examples:
*** CONTINUOUS SCRATCH TEST**
*** CRACK INITIATION LOCATION**
*** CRACK PROPAGATION**

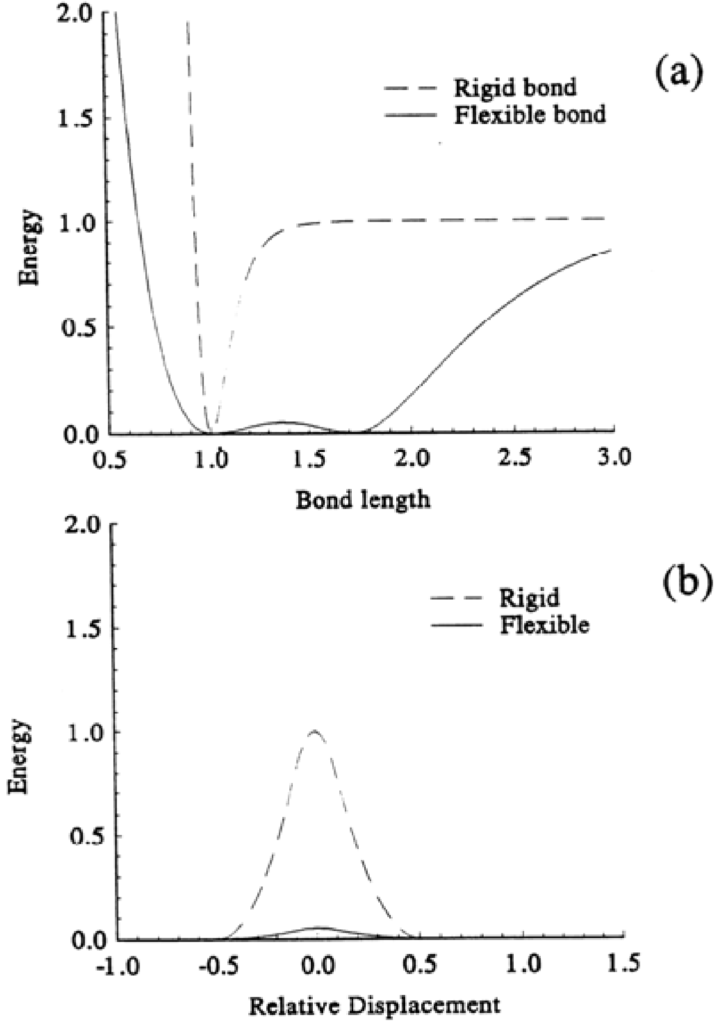
CAPABILITY TO CREATE MATERIALS WITH VIRTUALLY ARBITRARY STRUCTURES - INCLUDING MATERIALS WHICH DO NOT EXIST YET

CAPABILITY TO TEST EXACTLY THE ASSUMPTIONS OF MODELS AND THEORIES. IF A THEORY DOES NOT AGREE WITH SIMULATIONS RESULTS USING THE SAME SET OF ASSUMPTIONS, ONE CANNOT BLAME THE DISCREPANCY ON EXPERIMENTAL ERRORS

PRODUCTION OF RESULTS AT HIGH SPEEDS: we do not wait for the reagents to arrive, purification of materials, completion of processing, reaching thermal equilibrium, etc.

ISOLATING EFFECTS OF A SINGLE VARIABLE (see for instance W. Brostow, A.M. Cunha and R. Simoes, Polymer 2004, <u>45</u>, 7767).

There are several methods of simulation of materials, including Monte Carlo (convenient for equilibrium thermodynamic properties), Brownian dynamics (for instance for flow of polymer solutions) and molecular dynamics (MD).



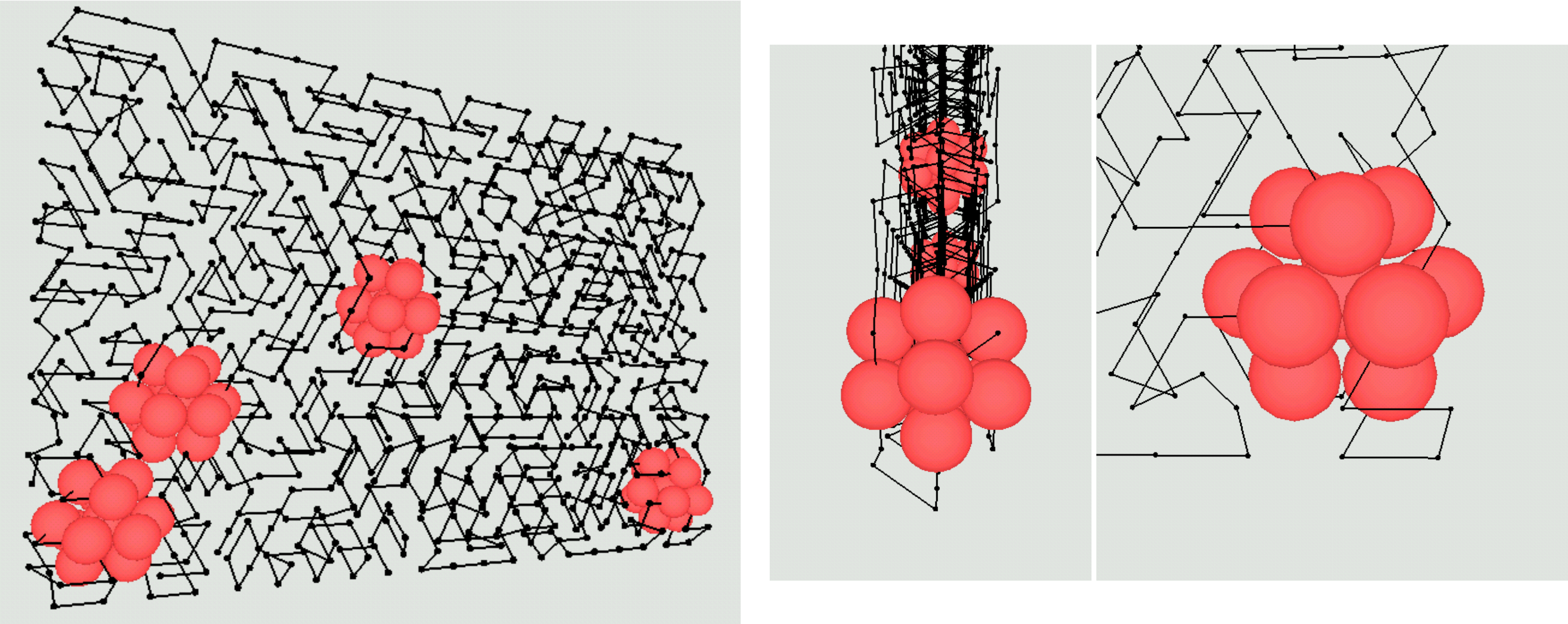
Potential energy of (a) bonding interaction between adjacent particles along a chain, and (b) repulsive interaction between neighboring particles on different chains.

We shall present here results obtained by MD simulations. Each particle (atom in a metal, a chain segment in a polymer, an ion) is characterized by 6 coordinates: 3 Cartesian coordinates of position and similarly 3 for momenta along the 3 Cartesian axes. Newton's equations of motion are solved at each time step. Interaction potentials between particles are defined, examples shown on the preceding page. An external force such as tensile can be defined in addition to forces corresponding to the interaction potentials.

We shall begin with simulations of tensile behavior of polymer liquid crystals (PLCs). These are two-phase systems, and the same approach can be used for other 2 (or more) phase systems. In PLCs the matrix contains mostly flexible (LC poor) chain sequences while the islands are rich in relatively rigid LC sequences.

As in any material, one wishes to know when and under what conditions the failure and fracture of the material occurs. The standard MSE method consists in applying scanning electron microscopy (SEM) to fracture surfaces and trying to figure out events which eventually led to fracture. This is an uphill battle. The same fracture surface can be reached by an infinite number of routes which all started with an undeformed material. By contrast, in simulations we can apply increasing forces gradually and observe <u>crack formation</u> as well as <u>crack propagation</u> and eventually the fracture. Related events such as crack arrest or crack bifurcation can be seen also.

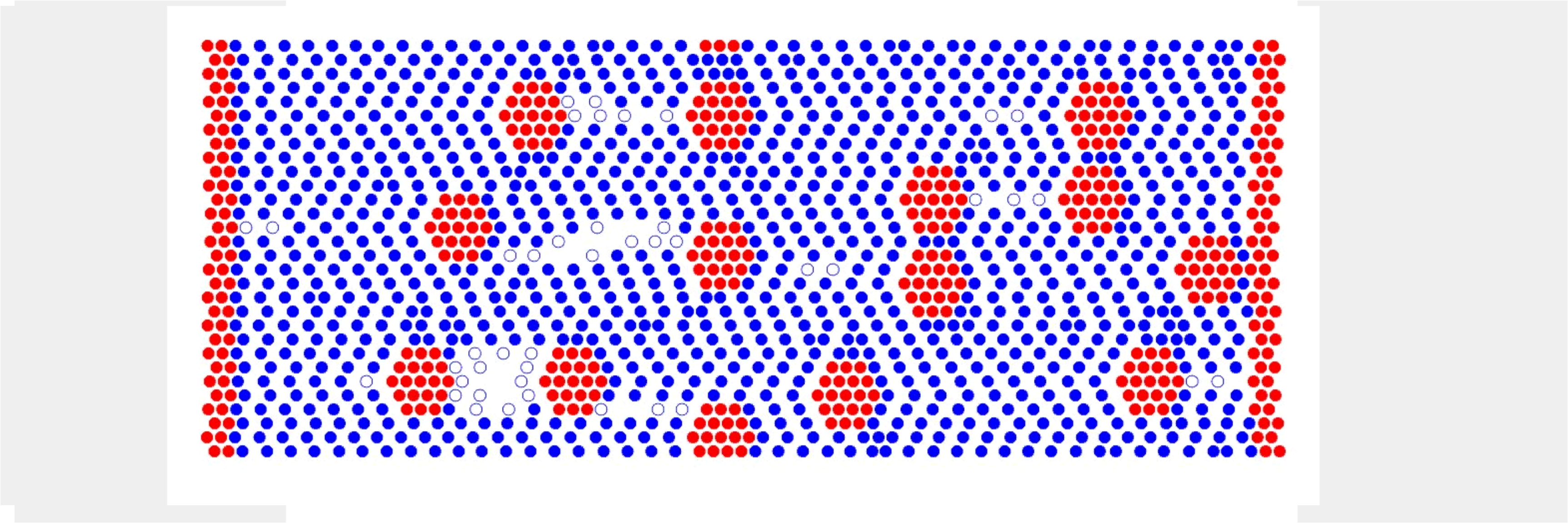
Two-phase systems



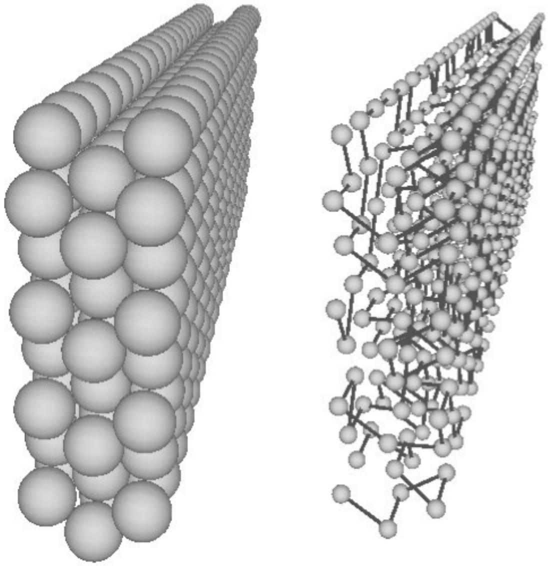
3D quasi-spherical island structure

Tensile deformation

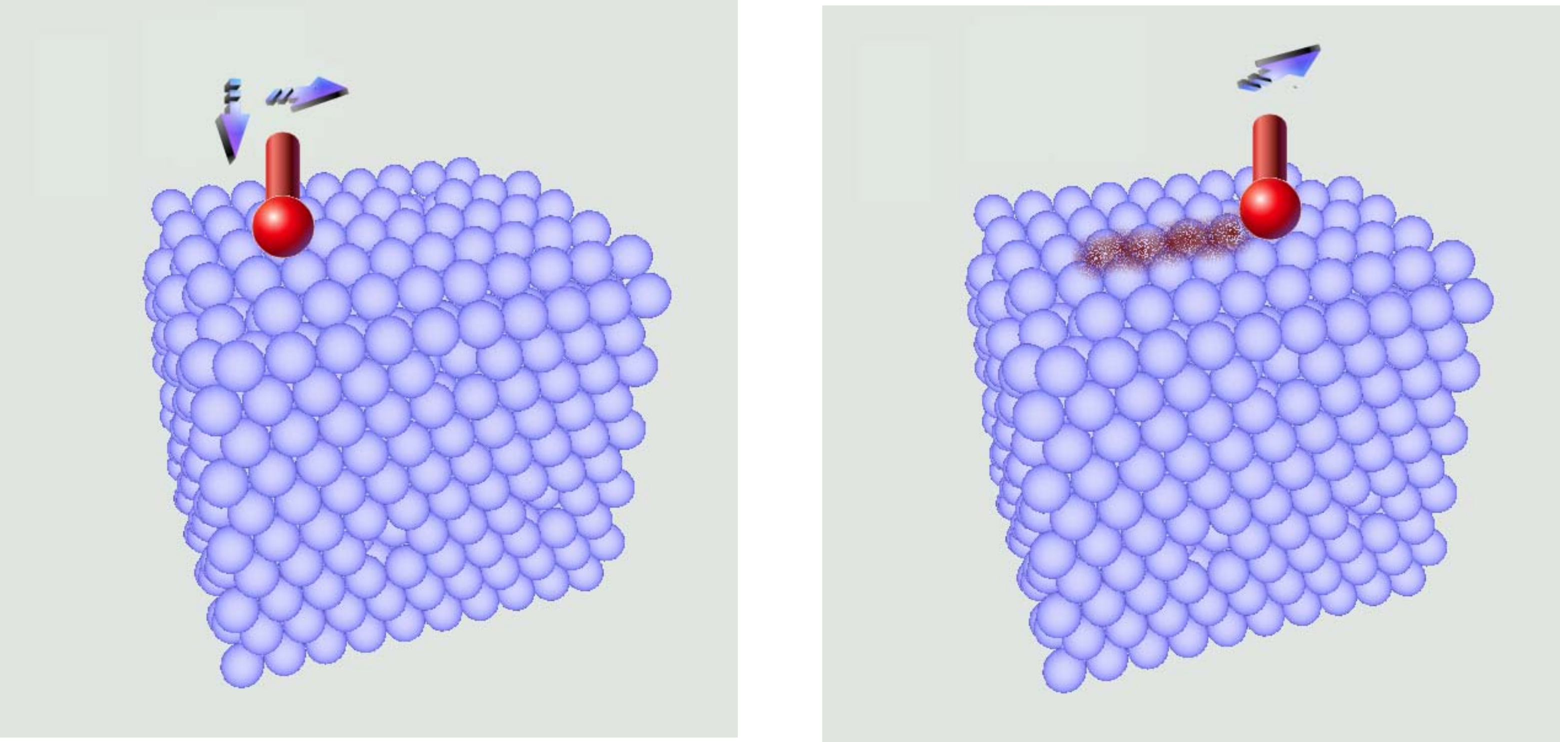
- Simulations allow us to pinpoint broken bonds and follow the development of cracks until fracture occurs



Rigid LC segments - red circles
Flexible segments - blue circles
Broken bonds - empty circles



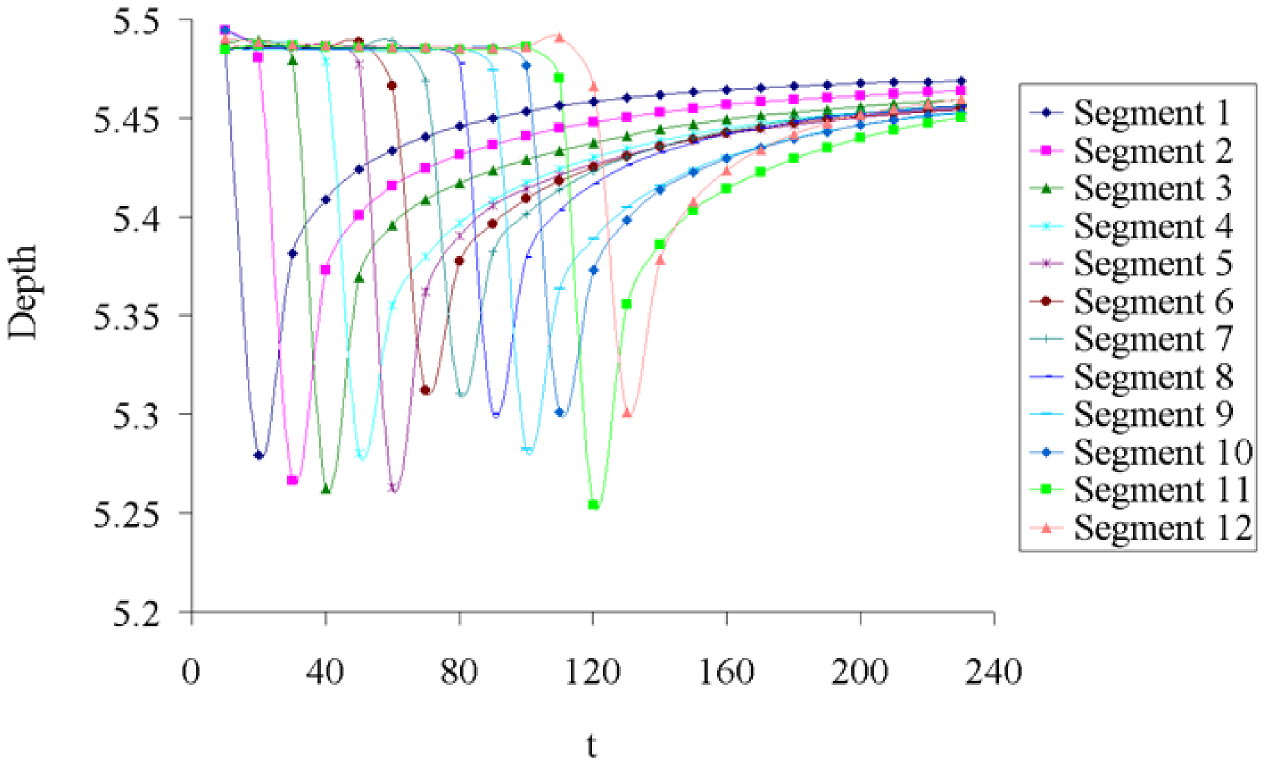
Side views of the specimen to be subjected to scratch testing. On the left side polymer chain segments are shown as spheres. On the right side connectedness of segments in chains is shown



Other views of performing the scratching simulations. The red element corresponds to the diamond indenter in experiments

The indenter advances against the surface of the material, scratches along that surface and is then removed before reaching the edge

Results of MD simulation of scratch testing



Experiments provide only 2 values, the average penetration depth (the bottoms of the curves) and the average recovery (healing) depth which is seen here as the asymptotic values. Simulations provide continuous dependence on time for each segment

Future of polymer tribology:

- As stated in the beginning, the most important for the improvement of tribological properties of polymer-based materials is the *understanding of fundamental mechanisms* which govern low friction, high scratch resistance and high wear resistance. The connection which has been shown of surface tension to friction and scratch depth is a step in this direction, but more such steps are needed.

- Improvement of tribological properties of polymer surfaces - generally much softer than those of metals and ceramics has to proceed along several lines. Using additives or fillers is only one of those lines, as is magnetic field application.

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