

## **TRIBOLOGY WITH EMPHASIS ON POLYMERS: FRICTION, SCRATCH RESISTANCE AND WEAR**

Witold Brostow<sup>1</sup>, Jean-Laurent Deborde<sup>2</sup>, Magdalena Jaklewicz<sup>3</sup> and Przemyslaw Olszynski<sup>4</sup>

<sup>1</sup>Laboratory of Advanced Polymers and Optimized Materials (LAPOM), Department of Materials Science and Engineering, University of North Texas, Denton, TX 76203-5310, USA; [brostow@unt.edu](mailto:brostow@unt.edu); <http://www.unt.edu/LAPOM>

<sup>2</sup>LAPOM; now at Lehrstuhl für Werkstoffe und Nanoelektronik, Ruhr Universität, Gebäude IC 2/144, D-44780 Bochum, Germany

<sup>3</sup>Department of Mechanical and Industrial Engineering, Concordia University, 1455 Blvd. de Maisonneuve West, H1441 Montreal, P.Q., Canada H3G 1M8

<sup>4</sup>Centre for Polymer Science and Technology, Department of Physics and Astronomy, University of Leeds, Leeds LS2 9JT, United Kingdom

### **ABSTRACT**

We provide the foundations and discuss the importance of Tribology in Materials Science and Engineering, with emphasis on Polymer Science and Engineering. We propose a characterization methodology and explain methods of determination of static and dynamic friction – implementable with a simple mechanical testing machine. We provide an example of friction results for a polymer system of the thermoset + thermoplastic blend type. We describe the key methods to characterize scratch resistance (penetration depth, scratch recovery) - applicable to all classes of materials. We provide examples of scratch testing results for a bare human tooth and also for a polymer liquid crystal subjected to magnetic fields. A recent quantitative measure of wear based on multiple scratching is discussed. Finally, we provide an instructive example how tribology has been used to create an ingenious medical device: there is friction when needed to assure the integrity of the device and virtually no friction when the planned decomposition of the device takes place.

**Keywords:** *friction, scratch resistance, viscoelastic scratch healing, wear determination, non-reusable syringe, polymer tribology, nanohybrids*

### **INTRODUCTION**

Tribological characterization of materials deals with *friction, wear, scratch resistance* and *design of interactive surfaces in relative motion*.

*Lubrication* is sometimes also considered as a constituting element but it can be included in the design, particularly so to affect friction and wear.

Let us consider Tribology from the point of view of the *materials user*. Gradual replacement of metals parts by polymeric components takes place in several industries, notably in automotive and aerospace manufacture. The use of polymer-based materials in dentistry is increasing. Thus, the need for understanding the tribological behavior of polymers is evident – as are the consequences of this fact for Polymer Science and Engineering (PSE) and more generally for Materials Science and Engineering (MSE) instruction.

A key book reflecting the contemporary status of PSE in the world has been created by J.E. Mark<sup>1</sup>. In the subject index of his book items such as tribology, wear, friction and scratch resistance are absent. The same statement applies to both the book by Goldman<sup>2</sup> who discusses thoroughly polymer deformation modes, and also to the highly useful book by Lucas and her colleagues<sup>3</sup> on characterization of polymers. On the other hand, there is a book by Rabinowicz<sup>4</sup> who has thoroughly covered the current status of tribology; his book deals with metals almost exclusively. Clearly tribology is well developed for metals but not for polymers. At the same time, even tribology of metals is not often an integral part of MSE instruction. There exists also ceramics tribology – necessary in the industrial process of machining where substantial tribological data exists for metal cutting and ceramic tooling, e.g., tool wear, lubrication methods, etc.<sup>5</sup>.

There is an important reason why Polymer Tribology has been developed so little: it is difficult. To give just one example, in carbon-fiber reinforced polymers the presence of fibers lowers the wear resistance of the neat polymers<sup>6</sup>. *A priori* one would expect the opposite effect, the fibers enhancing the wear resistance. A chapter on polymers in a collective Swiss book on tribology<sup>7</sup> consists mostly of tabulated and diagrammatically presented friction values.

In the following Section we define the basic concepts as well provide examples of tribology and its applications.

## BASIC CONCEPT OF TRIBOLOGY

While metallurgy has been in existence for thousands of years, even in Metallurgy courses tribology is included only briefly – if at all. Therefore, we now discuss key concepts of tribology.

The science of *Tribology* (Greek *tribos*: *rubbing*) concentrates on contact mechanics of moving interfaces that generally involve energy dissipation. This is why tribological characterization of material deals with adhesion, friction, wear, lubrication, scratch resistance and design of interacting surfaces in relative motion.

*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.

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

where  $N$  represents the normal force and  $\mu$  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<sup>8</sup> – 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.

This relationship is commonly referred to the first laws concerning friction formulated in 1699 by Amontons<sup>9,4</sup>, namely:

- a) the resistance caused by friction is proportional to the load;
- b) that resistance is independent of the apparent area of contact.

The useful life of components which function in tribologically demanding environments is

governed by the *wear*. This is usually quantified by evaluating the specific wear rate

$$u_{sp} = V_{loss} / (F \cdot D) \quad (2)$$

where  $V_{loss}$  represents the volumetric loss of the sample,  $F$  the force applied and  $D$  the total sliding distance. Eq.(2) serves as an introduction to the subject, we discuss wear more in detail in Section 6.

*Scratch resistance* is one of the most important service parameters. A contemporary method of its determination is defined in Section 5, but let us now provide a chronological introduction to this area. Historically, a scratch test was originally designed as a measurement of adhesion of thin hard films. The test was first proposed by Heavens in 1950<sup>10,11</sup> and implemented in 1960 by Benjamin and Weaver<sup>12</sup> who were also responsible for developing the first model of the phenomenon. However, their model failed to describe the behavior of hard coatings. The scratch test consists of deforming the surface by indentation under load of a moving hard tip. The applied load can be held constant, increased continuously, or increased stepwise. The smallest load at which the coating is damaged is called *the critical load*  $L_c$ . One notices that the phrase "is damaged" is not quantitative.

In 1985 Steinmann and Hintermann<sup>13</sup> used a scratch test method that relied upon an acoustic emission (AE) signal to determine the critical loads for TiC deposited by chemical vapor deposition upon various substrate materials. Their scratch test method reported data as AE versus load graph. This provides a certain capability to determine the critical load  $L_c$ , either as a point where a strong acoustic signal appears, or else as the maximum of the resulting peak. However, there is a trap here; if we have a polymeric thin film on a hard ceramic substrate, there will be a strong acoustic signal when the hard tip reaches the bottom of the film and begins to scratch the ceramic. At this point the film is not only "damaged" but cut into two. However, AE does have a role also in contemporary scratch determination (Section 5).

Kody and Martin developed a fairly sophisticated scratch testing methodology in 1996<sup>14</sup> which involves quantifying the light scattered from solid polymer or a polymer composite surface due to surface deformation. The technique involves first deforming the material in a controlled and reproducible manner. The machine uses a conical diamond stylus to induce scratches into a flat piece of material mounted on a rotating stage. The results could then be used to compare the scratch resistance of materials with different compositions and different textures.

We have noted in the beginning the trend to switch from metallic to polymeric parts in several industries. The main reason in the automotive and aerospace industries is energy saving. Densities of polymers are generally lower than those of metals. For a given amount of fuel, a car with more polymer-based components can cover a larger distance than a heavier car with more metal parts. Yet, as already argued above, our understanding of tribology of polymer is hardly sufficient. Needless to say, frictional properties of plastics differ markedly from those of metals.

Ceramics are largely brittle so that even shallow scratches followed by a deformation can result in fracture. Using *lubricants* can provide friction lowering as well as protection against scratching and wear for metals and ceramics but not so for polymers; see more on this in Section 6.

## MATERIALS PREPARATION

As in other areas of materials characterization, the experimental materials should be prepared and characterized by a predefined procedure. The standards followed should be quoted – although tribology has a relatively small number of standards in existence, much less than mechanics. All samples studied should have the same thermal history. To avoid the possibility of degradation by moisture or other agents in the material environment, an appropriate storage method should be applied.

It is worthwhile to make a list of factors affecting tribological properties of polymers<sup>15</sup>: structure and position of macromolecules on the surface; multiphasicity; degree of crystallinity; kind of polymers, such as homopolymers, block copolymers, etc.; composition for blends; chain orientation acquired in processing such as extrusion; molecular structure such as linear, branched or crosslinked; and molecular mass distribution since short chains tend preferentially to surfaces.

## FRICITION DETERMINATION

### Machine

For the static and dynamic friction determination there is an ASTM standard<sup>16</sup>. The testing machine should permit the use of a moving sled - on which the parallelepiped sample is attached - with a stationary plane; see Figure 1. The standard<sup>16</sup> allows also the opposite option, namely the use of a stationary sled with a moving plane. In the option shown in Figure 1, the sample fixed on the back of the sled slides over the surface of the plane creating a friction resistance.

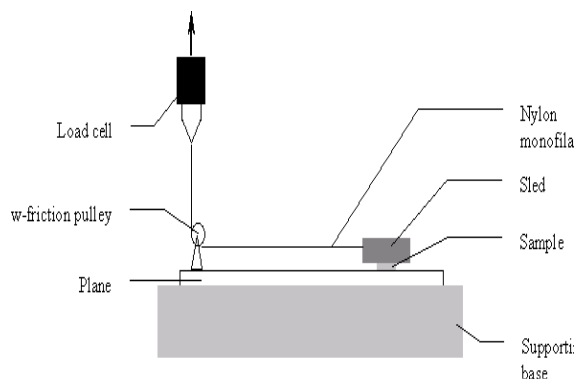


Figure 1. Assembly for the friction test.

The D 1894-90 standard specifies the speed of 150 mm/minute, the temperature of  $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$  and  $50\% \pm 5\%$  relative humidity. In practice we also use lower speeds to achieve high accuracy in relatively small specimens.

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

standard<sup>16</sup> also defines *slip* by a cautious statement: "In a sense, it is the antithesis of friction". For metal and ceramic surfaces slip can be enhanced by using lubricants.

### Test conditions

An environmental chamber should be used if needed to maintain isothermal conditions. The load cell should be appropriate to force existing in the system and a sled should have the nominal weight meeting the standard requirements. A co-specimen should be defined, such as aluminum stationary plane for a sample moving on a sled. Generally at least 10 runs should be performed and the results reported should be quoted together with the appropriate statistical information.

### An example of friction results

In our work we use a SINTECH universal testing machine from MTS Systems Corp., Eden Prairie, MN, USA, to determine the friction characteristics. The tests are performed at the room temperature of  $24^{\circ}\text{C}$ . A 44.6 N (10-lb.) load cell and a sled with the nominal weight of 700 g are used. A Teflon co-reference specimen is used.

Earlier in this Journal we have discussed a wide range of applications of epoxy thermosets<sup>17-19</sup>. We are working on extending this range still further<sup>20-22</sup>.

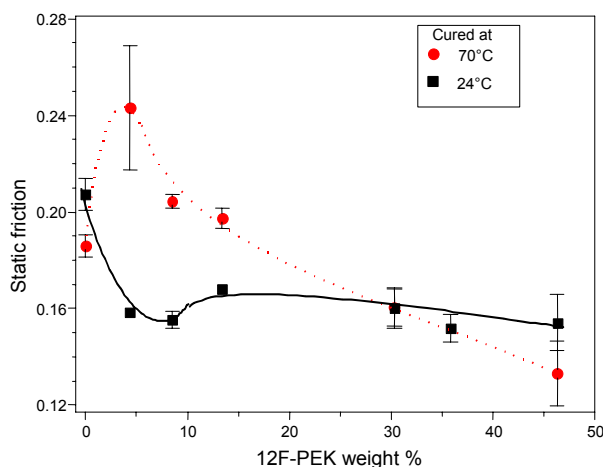


Figure 2. Static friction in the epoxy + 12F-PEK system as a function of the weight percentage of the fluoropolymer; after Ref. 20.

Figure 2 shows results obtained for a commercial epoxy crosslinked by a curing agent in the presence of varying concentrations of a fluoropolymer (fully fluorinated poly(aryl ether ketone), 12F-PEK)<sup>20</sup>. The curing was performed at two different temperatures. The results shown in Figure 2 are averages of 15 - 40 tests each.

We see in Figure 2 that for instance the addition of 2.5 weight % of the fluoropolymer *increases* static friction for the material cured at 70°C but *decreases* the friction when the crosslinking was performed at 24°C. The results for dynamic friction reported in<sup>20</sup> are similar. Thus, not only the composition but *also the thermal history* determine tribological properties. It is because of this situation that we have developed an equation for the progress of curing (crosslinking) as a function of both time and temperature<sup>23</sup>. In the case shown, the fluoropolymer “swims” to the surface to lower its friction at 24°C. At 70°C the curing is faster; the curve of the viscosity vs. time has its minimum earlier. As a consequence, much smaller amounts of the 12F-PEK thermoplastic have the time to reach the surface, they only perturb the surface of the epoxy and increase the friction.

## SCRATCH RESISTANCE DETERMINATION

### Machine, experimental procedure and calculations

A scratch test method involves scratching the surface of samples and measuring the depth of the groove while the scratch is being made. This can be done under either a constant load, or a progressively increasing load, or else under a stepwise increasing load. The resulting values are called the *penetration depth* and we represent them by the symbol  $R_p$ . Since polymers are viscoelastic materials, they should recover or heal after the scratch, with the bottom of the groove going up and settling at a final level called the *residual depth*  $R_h$ .

After a world-wide analysis of the equipment available, we have chosen a Micro Scratch

Tester (MST) from CSEM Instruments, Neuchatel, Switzerland. A schematic of this machine is shown in Figure 3; it has the depth resolution of  $\pm 7.5$  nm. Since the typical scratch depths are of the order of hundreds of microns, the accuracy is better than required by several orders of magnitude.

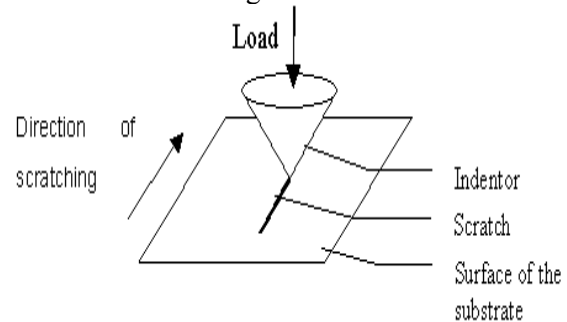


Figure 3. Assembly for the scratch test.

The machine shown in Figure 3 is usable for testing all classes of materials.

In the experimental procedure, a diamond tip generates a controlled scratch on the surface of the sample. The indenter type should be defined. Each run includes a pre-scan; it serves for the characterization of the topology of the sample before the scratch is made. The pre-scan involves application of a very small constant force; we denote the vertical coordinates so determined as  $R_0$ . Then follows the measuring scan ( $R_p$  determination), which is in fact the determination of the current vertical coordinate at a given point after subtracting  $R_0$  from it. The secondary measuring scan (post-scan) determination gives  $R_h$  by a similar subtraction of  $R_0$ . A minimum number of scratches should be defined for each sample under constant load; results reported should be averages. The velocity of scratching should be chosen as well as the scan length. The time when the post-scan is performed should be established. In our experience 3 minutes are sufficient for viscoelastic recovery for the materials we deal with, but we determine  $R_h$  after 5 minutes. The apparatus we use measures also the tangential frictional force, provides an acoustic signal and the capability to observe the sample under an optical microscope. The Micro Scratch Tester is controlled from a personal computer and the software collects and displays the results. The acoustic signal is also generated; as discussed

above, it provides a particularly pronounced signal when the indenter encounters a different phase.

Comparison of the two depths should provide *the amount of healing or recovery* the surface has experienced after the scratch - which therefore we have defined<sup>22</sup> as

$$\Delta R = R_p - R_h \quad (3)$$

Polymers often heal well, the residual depth is much less than the initial penetration depth, resulting in relatively high  $\Delta R$  values. The percentage recovery can be calculated<sup>22</sup> as

$$\phi = (\Delta R/R_p) \cdot 100 \% \quad (4)$$

### Examples of scratch testing results

We have obtained scratch testing results for the same series of epoxy + 12F-PEK compositions<sup>22</sup> for which friction results are shown in Figure 2. We also have results for instance for a thermoplastic epoxy called BLOX<sup>24,25</sup> the scratch resistance of which was improved by addition of other thermoplastics<sup>26</sup>. However, to display the generality of the technique, in Figure 4 we display the penetration depth and the recovery depth for a human molar tooth extracted from a volunteer<sup>27</sup>. The measurements were carried with the Micro-Scratch-Tester at the constant load of 5 N, the groove length = 2 mm, the scratching velocity 5.3 mm/minute; a 200  $\mu\text{m}$

radius diamond tip was used.

The objective of this particular study was to determine the effects of nanohybrid coatings on scratch resistance. *Nanohybrids* are formed either by a chemical reaction between the inorganic and organic constituents or else by mixing components on the nanoscale level so that particles of a constituent (for instance inorganic) in a matrix of the another material are no larger than 100 nm in diameter<sup>28</sup>. Nanohybrids are clearly different from heterogenous composites (HCs) that is materials in which constituents of several kinds are combined together at the macroscopic level<sup>29</sup>. Fiber-reinforced plastics are typical HCs.

To have a reference for the results of using nanohybrid coatings, we have started with “naked” teeth scratched perpendicularly to the growth direction. As an incidental result, we have found how irregular the “smooth” teeth surfaces are. An example of results of applying our nanoscratch tester to a bare tooth are shown in Figure 4. The Figure shows an important result: the bone surface exhibits viscoelasticity in tribological behavior<sup>27</sup> – similar to that of polymeric materials but unlike metals and ceramics. We have also investigated a number of metal and inorganic oxide ceramic surfaces (unpublished results) but we have found only negligible amounts of viscoelastic recovery.

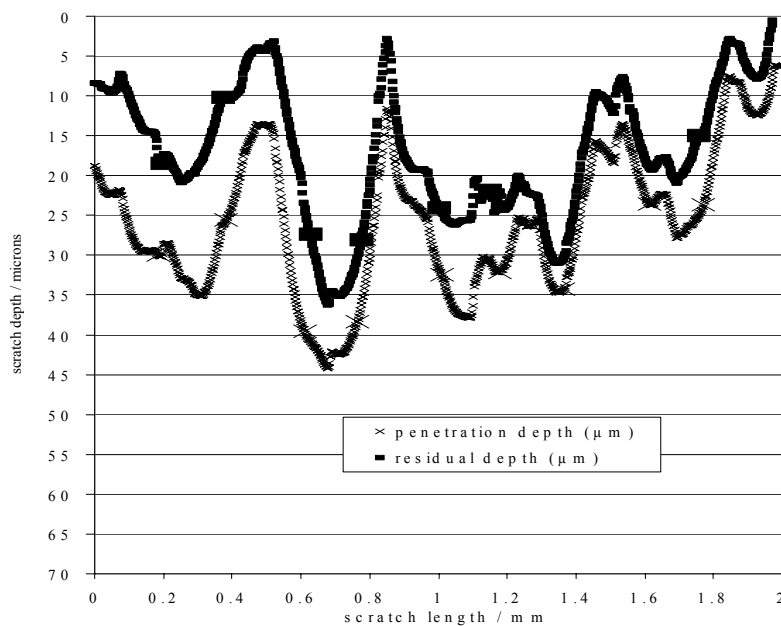


Figure 4. Penetration depth  $R_p$  and recovery depth  $R_h$  of a human tooth as a function of location along the scratch path; after Ref. 27.

A bone (including a tooth) is a noncomposite of hydroxyapatite and an organic matrix, with collagen as the main component of the latter<sup>30,31</sup>. The amount of healing  $\Delta R$  as defined by Eq. (3) and seen in Figure 4 is significant. Thompson and coworkers<sup>32</sup> explained the bone viscoelasticity seen in *mechanical* tests in terms of re-formation of sacrificial bonds. The *tribologica I* results reported in<sup>27</sup> at least agree with this explanation.

Since in general the material orientation affects the properties, this should apply also to tribological properties. For example, polymer liquid crystals (PLCs) have a much wider service temperature range than engineering polymers (EPs), better mechanical properties, low thermal expansivity, resistance to ultraviolet radiation and other advantages<sup>33,34</sup>. Typically, orientation is introduced by shearing fields in processing such as injection molding or extrusion.

However, we can also introduce orientation by imposition of a magnetic field<sup>33,35</sup>.

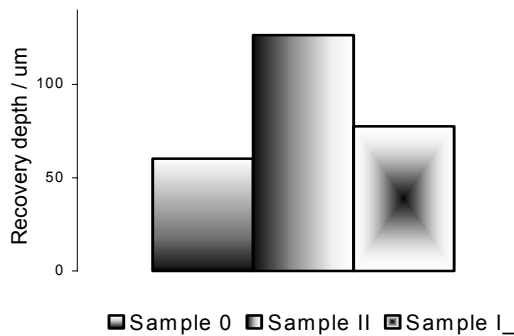


Figure 5. Recovery depth  $R_h$  of a polymer liquid crystal (see text) as a function of imposition (or otherwise) of a magnetic field and direction of scratch test with respect to the field orientation after Ref. 36.

In Figure 5 based on results reported in<sup>36</sup> we compare determinations of recovery  $\Delta R$  defined by Eq. (3) for a polymer liquid crystal (PET/0.6PHB, a copolymer of poly(ethylene terephthalate) and p-hydroxybenzoic acid, the mole fraction of the latter = 0.6). We see the result for a sample not subjected to the magnetic field (left), subjected to the field and

scratched along the field direction (center) and subjected to the field and scratched perpendicularly to the field direction (right). The alignment was achieved at 280°C (the melting temperature of PET/0.6PHB = 200°C) under the exposition to the 1.8 Tesla field for 30 minutes.

We see that the sample scratched along the orientation direction shows the highest amount of healing  $\Delta R$ , the sample which was not exposed to the field the lowest, and the sample oriented in the field but scratch tested perpendicularly to the field direction has an intermediate value. To explain these results, see Figure 6<sup>36</sup>.

In part *a* of this Figure we see relatively small and circular LC-rich islands. The islands offer relatively little resistance to the scratching diamond, hence relatively deep penetration depths  $R_p$ .

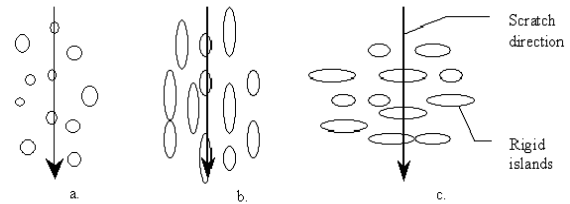


Figure 6. Morphology of the polymer liquid crystal with and without magnetic field imposition and scratch direction with the respect to the field orientation; after Ref. 36.

At the same time, small islands have relatively low scratch recovery capability – as seen in Fig. 5a. In Figure 6b we see that the magnetic field has created larger islands. Therefore, there is more resistance against the motion of the diamond indenter which is reflected in shallow penetration depth  $R_p$ <sup>36</sup> and high recovery in Figure 5b. The case in Figure 6c is intermediate. Islands are larger than those in Figure 6a, hence more resistance to the indenter (shallower penetration depth  $R_p$ <sup>36</sup>) and higher recovery (Figure 6c) compared to the sample not exposed to the magnetic field. At the same time, the fraction of the indenter trajectory which goes across the islands is lower than in the case b, hence intermediate results.

## WEAR

*Wear* can be defined as the unwanted loss of solid material from solid surfaces due to mechanical interaction<sup>4,37</sup>; see also Eq.(2) above. The definition implies that wear can be simply determined from the volume (or else from weight) of debris (also called wear particles) which separates from the specimen during testing. Either quantity can be made intensive (in the thermodynamic sense, that is independent of mass) by dividing the debris weight or debris volume by the contact surface of the specimen. Interestingly, we have not found in the literature discussions of deficiencies of the debris method - while in our opinion it cannot provide reliable results. The amount of debris depends on the relative velocity of the two surfaces in contact. A part of the energy of motion is converted into heat at the sliding or rolling surface. The higher the velocity, the more heat is generated. Thus, the experiments are anything but isothermal. Since polymer-based materials are viscolastic, temperature has large effects. We have found that frictional properties as well as scratch resistance are related to the surface tension of the polymer solid<sup>38</sup> which is also temperature dependent. According to heat capacities, the same relative velocity will produce different temperature increases in different polymers; even with the velocity constant throughout the experiments the results will not be entirely meaningful. Still further, consider two polymers with a large difference in their glass transition temperatures  $T_g$ . The heat generated during the test might move one material above its  $T_g$  while the other will remain in its glassy state. Comparison of the amounts of debris in this case will be even less meaningful.

To appreciate the economic importance of wear, let us quote from the book of Rabinowicz<sup>4</sup>: “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. At the time the Jost Report appeared it was widely felt that the Report greatly exaggerated the savings that might result from improved tribological expertise. It has now become clear that, on the contrary, the Jost Report 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.”

Later on in his book Rabinowicz discusses methods of wear characterization<sup>4</sup>. While he describes the debris method, he provides more space to an electric resistance method. Needless to say, determination of electric resistance is well usable and accurate for metals – but not in general. He also suggests measuring the width of the scratches but points out that this method “appears to have been used only in a qualitative way”. It seems that none of the extant methods of wear determination has received a general acceptance.

Similarly as with friction, wear is much better understood for metals than it is for polymers<sup>4,39,40</sup>. An 840 page book on polymer testing does not even have the word “wear” in its subject index<sup>41</sup> although surface wear is important in industry<sup>42</sup> as well as in medical applications of polymers<sup>43</sup>.

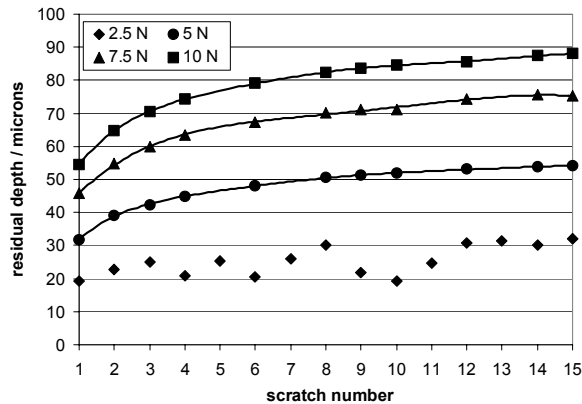
In general, the connectedness of atoms makes direct application of metal tribology to polymers doubtful. Goldman and his coworkers have shown how important entanglements are for mechanical properties of polymers<sup>44</sup>. It would be surprising if an analogous statement did not apply to tribological properties. In recent years numerous attempts have been made to connect *hardness* to wear. The results are either not very meaningful or even contradict other results along similar lines. There are at least two reasons for this. First, there is a large number of hardness tests<sup>37</sup>; material A will be harder than material B in test X, but softer than material B in test Y. Second, when performing one kind of test only, we can find that material C is harder than D, and at the same time there is less wear in C; such a case would confirm the idea of a proportionality of some sort between hardness and wear. However, we can also have



material E harder than material F, but F undergoes *less* wear because E is brittle.

Thus, neither PSE nor MSE as a whole provide a single and reliable procedure for determination of wear. Therefore, we have developed a method which we expect will serve as a measure of wear; it involves using the micro scratch tester in the *multiple* scratch determination mode<sup>45</sup>.

Figure 7 shows the results of such an experiment. We display the residual depth  $R_h$  as a function of the number of scratches made for teflon (polytetrafluoroethylene, PTFE)<sup>45</sup>. The depth has been determined at 2.5 mm from the origin, that is in the middle of the scratching range (in all runs the full range was 5 mm). The results at the lowest force of 2.5 N show considerable scatter; we are clearly below the force level at which reliable results can be obtained. However, for the higher force values we see that each residual depth curve reaches



an asymptote.

Figure 7. Wear determination by multiple scratching: residual depth  $R_h$  for Teflon as a function of the scratch number at four different loads; after Ref.45.

The results displayed in Figure 7 are somewhat reminiscent of *fatigue*<sup>37</sup>: mechanical loading to a relatively low level but multiple times eventually leads to fracture. We see in the Figure that consecutive scratch tests produce gradually diminishing deepening of the scratch bottom, leading eventually to a depth which does *not* change with the number of scratches made.

We presume that a phenomenon akin to work hardening in metals takes place; the bottom of the scratch “valley” after several runs represents a high cohesion material. Thus, we can define<sup>45</sup> a measure of wear  $W(L)$  for a given indenter geometry and load  $L$  as

$$W(L) = \lim_{n \rightarrow \infty} R_h(L) \quad (4)$$

where  $n$  is the number of scratch tests performed. As seen in Figure 7, 15 tests seem to be sufficient, although more tests than 15 have also been made to see whether any further changes occur<sup>45</sup>. We actually stop the tests when the quantity  $[R_h(n+1) - R_h(n)]/R_h(n)$  amounts to less than 1%.

There is also at least one more option along these lines: establishment of an asymptote for large loads, that is

$$W = \lim_{L \rightarrow \infty} W(L) \quad (5)$$

Thus, if such an asymptote exists, the quantity defined by Eq.(5) would be independent of both  $n$  and  $L$ . We shall see whether our suggestions embodied in Eqs.(4) and (5) will gain wider acceptance.

The results presented in Figure 7 confirm also facts in tribology known to every cook: teflon has low friction but very poor scratch resistance. We see that the asymptotic residual depth  $R_h$  for the 10 N load is  $\approx 88$  microns. The corresponding value for polypropylene is  $\approx 43$  microns<sup>45</sup>, that is less than half the depth for PTFE.

Take two viscoelastic materials, one with higher dynamic friction than the other. It is expected that the material with higher friction will also exhibit higher wear. We also recall the connections between both kinds of friction, scratch resistance and the surface energy of polymer solids which we have found for epoxy + fluoropolymer systems<sup>38</sup>. Still further, since scratch recovery is viscoelastic, determination of viscoelastic properties is clearly worthwhile. As eloquently demonstrated by Menard<sup>46</sup>, dynamic mechanical analysis is the best way to determine viscoelastic properties. The storage modulus  $E'$  and the loss modulus  $E''$  can be measured as a function of frequency  $\nu$  of the

sinusoidal force imposed on the material and also of temperature.  $E'$  represents the elastic solid-like constituent of the response of the viscoelastic material while  $E''$  represents the viscous liquid-like response. In view of the results already accumulated, we intend to pursue connections between  $W(L)$ ,  $W$  (see again Eqs.(4) and (5)),  $E'$ ,  $E''$ , static and dynamic friction and also surface energy of polymer-based materials. The use of rubberized surfaces for conveyor systems that handle abrasive materials might be explicable in those terms. The rubbery state is characterized by low storage modulus  $E'$ . The conveyor rubber adapts easily to the shapes of the pieces conveyed so that the pieces are transported with only little movement with respect to the original drop location.

The final question on wear is of course: how can we diminish it? In the beginning of this article we mentioned the results reported in<sup>6</sup>; carbon fiber reinforcement has increased the volumetric debris wear of polyetheretherketone (PEEK). However, the behavior of the PEEK + carbon fibers is not necessarily universal. Methods of increasing adhesion between the reinforcing fibers and the polymer matrix are being developed, such as oxygen plasma treatment of carbon fibers developed by Springer and his coworkers<sup>47</sup>. The same group has developed methods of modification of natural fibers of sisal and coir by dewaxing, alkali treatment and methyl methacrylate grafting<sup>48</sup>. Furthermore, for a polymer liquid crystal, Chen and Springer have shown that the molecular arrangement of LC units in a comb PLC (with LC units in side chains) on the polymer surface depends on the sorbed  $N_2$  or  $CO_2$  molecules<sup>49</sup>. Thus, one can make a list of options available to decrease wear<sup>50</sup>:

- a) external lubricants. This method is of course widely used in metals, but in polymers it is limited to those cases only when the lubricant does *not* cause swelling of the polymer;
- b) internal lubricants. We have used them to advantage in LAPOM (unpublished results);
- c) fiber reinforcement – provided good adhesion of the fibers to the polymer is achieved<sup>47</sup>;

- d) reinforcing fiber modification<sup>48</sup>;
- e) chemical modification of polymers - including thermosets<sup>21</sup>;
- f) physical modification by blending<sup>20,22</sup> on the basis of connections between scratch testing and wear; see again Eqs.(4) and (5). Along these lines, poly(vinylidene fluoride) + ultra-high molecular weight polyethylene + carbon black systems developed by Mirony and Narkis<sup>51</sup> have also been investigated. Enhancement of polymer scratch resistance by the presence of carbon black and also by  $\gamma$  irradiation resulting in crosslinking has been found<sup>52</sup>;
- g) magnetic field modification<sup>36</sup>; see again Figure 5;
- h) the use of protective coatings - such as nanohybrids which increase the scratch resistance of human teeth<sup>27</sup>.

## FRICION AS AN ADVANTAGE

Above we have described some ways to lower friction of surfaces. To get an overall picture of the situation, let us describe a case in which the existence of friction is advantageously used to construct a highly original device.

The problem was the development of a non-reusable hypodermic syringe. Many communicable diseases are commonly spread by contacting body fluids of an infected person. Reuse and sharing of hypodermic syringes is a typical way such contact occurs; the problem is particularly acute among drug users. Here lies a major cause for spread of AIDS: when accidental needle sticks from needles used on infected patients occur<sup>53</sup>. This affects medical personnel, sanitation employees, others in the syringe disposal chain, and through all these routes the general population. Thus, the problem is by no means limited to drug addicts.

The problem was solved in a series of patents invented by Thomas J. Shaw<sup>53,54</sup>. Essentially the same principle is used in a dental syringe<sup>55</sup>. Outside the syringe is quite similar to the traditional ones, the medication is dispensed through a needle into the body of the patient.

However, in this particular design the plunger is depressed further into a smaller diameter nose portion at the time point when all medication has just been dispensed. The nose portion contains a compressed spring. The additional depression requires somewhat more thumb force against friction - but releases the spring which pushes the polymeric needle holder and the needle backwards. In this way friction is the ally of the injection procedure – preventing premature needle retraction before the medication has been dispensed fully. Retracting, the needle breaks the vacuum with the skin, so that undesired blood and body fluids are not extracted from the patient as the needle is removed. Moreover, when retracting, the needle holder and the needle are not in substantial contact with the syringe seal; practically there is no friction to be overcome, the needle moves backwards and “settles” inside the now empty central compartment occupied before by the liquid medication. Since the spring was originally outside that central part, there was no contact between the spring material and the medication to be injected.

Details can be found in the patents quoted, and there are also related patents for catheters and systems for fluid collection from patients. The syringe is indeed completely non-reusable. In this example, Polymer Tribology plays a dual role in an ingenious and original way: there is friction when needed to assure the integrity of the device and virtually no friction when the planned decomposition of the device takes place.

While much remains to be done, the results surveyed above show that originality is the main factor in creating materials and components with improved tribological properties for new and extended applications. Teaching more Tribology - including Polymer Tribology - seems a very good way to attract more engineers and scientists to this important area.

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