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TRIBOLOGY OF POLYMERS AND POLYMER-BASED COMPOSITES

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ABSTRACT

While attention of academia and industry on materials properties is largely focused on mechanics, *wear* causes losses in industry at least not smaller than fracture caused by mechanical deformation. We discuss the importance of tribology for polymer-based materials (PBMs). Traditional tribology developed originally for metals cannot be applied to PBMs for at least two reasons. First, PBMs are viscoelastic and their properties depend on time – in contrast to metals and ceramics. Second, external liquid lubricants, which work well for other classes of materials, are easily absorbed by PBMs; swelling is the result. We and others are developing tribology of PBMs taking into account among others: viscoelasticity, materials brittleness defined in 2006 and connections of brittleness to recovery in sliding wear determination, relation of friction and scratch resistance to surface tension, and effects of magnetic fields on polymer tribology. Traditional experimental methods of wear determination based on the amount of debris formed are not well usable for PBMs since often there is no debris - while there is significant material displacement (top ridge formation, densification). More appropriate testing procedures are discussed. Results of molecular dynamics computer simulations of scratching of polymers are discussed also. Further, we discuss methods of enhancing resistance of PBMs to scratching and wear. These methods include modifying surface tension, formation of microhybrids, formation of nanohybrids, irradiation, as well as already mentioned application of magnetic fields. On the basis of the totality of experimental and simulation results as well as concepts and models developed, some recommendations for dealing with tribology of PBMs – in instructional as well as industrial and research setting - are made.

Key words: *tribology of polymeric materials, friction and wear, multiple scratching, brittleness, viscoelasticity, micro-tribology, nano-tribology*

1. INTRODUCTION

The present article provides an extension and update of a 2003 article in the same Journal[1]. Tribology deals with relative motion of surfaces. It involves friction, wear of materials, scratching and rubbing. A more pedantic definition describes tribology as a science and technology of surfaces that are in contact and relative motion, as well as supporting activities that should reduce costs resulting from friction and wear[2,3]. Economic consequences of materials' wear are clearly described in the Rabinowicz book[4] – quoting a report to the British Government of 1966 when the word 'tribology' was used for the first time[1]. Increasing applications of polymeric materials require knowledge of their tribological properties – different from much better understood tribological properties of metals and ceramics[4]. An important part of tribology deals with materials selection and surface processing inasmuch as they affect wear[3]. These facts deserve to be taken into account in instruction in Materials Science and Engineering, in industrial practice and in laboratory research.

Friction is the resistance to motion that occurs whenever one solid body is in contact with another solid body. *Wear* represents a surface damage or removal of material from one or both sides of solid surfaces that are in contact during motion. In most cases, the wear occurs by surface interactions on the surface irregularities. Wear and friction are not material properties, but the answer of a given tribosystem[3]. The purpose of the research in tribology is to minimize and remove losses that occur due to friction and wear at all levels, where rubbing, grinding, polishing, and cleaning of surfaces take place. Tribological parameters include surface roughness, mechanisms of adhesion, friction and wear, and physical and chemical interactions of lubricants (if present). Interacting surfaces must be understood for optimal function and long-term reliability of components and devices and economic viability. Basic understanding of the nature and consequences of materials' interaction at the atomic and molecular level leads to the rational design of materials for the specific applications. Micro- and nanotribology are new areas of tribology when one tries to improve tribological properties by using respectively fillers with sizes in the μm or nm range. Tribological *techniques* (equipment and methods) designed for testing on those small scales represent a growing area.

We shall talk in this review largely about polymers but also about polymer-containing composites. Together, these can be called polymer-based materials (PBMs).

From the viewpoint of materials users, it is advantageous to replace metal parts in various industries such as manufacturing of cars, airplanes, etc. by PBMs. The advantages include lower density, less need for maintenance, and also lower cost[5,6]. The main reason for the trend of replacing metal parts by polymers is energy-saving. Density of polymers is generally lower than the density of metals, so that with a certain amount of fuel the car with the polymer parts can travel greater distance compared with a standard car with mostly metal parts; the same applies to airplanes[4]. Application of polymers in dentistry and medicine is also on the rise[7]. Application of polymer coatings especially in the form of nanohybrids, containing for example carbon nanofibers provides improved properties[8,9]. Tribology of ceramics[4,10,11] and metals present in many industrial processes[11] is much more frequently described than is the case with tribology of polymeric materials[12-17]. It is known that the ceramic materials are very brittle, and that even shallow scratching may be accompanied by deformation that leads to fracture. That is why tribology is very important in the analysis of tool wear, lubrication procedures in industrial processing and particle separation processes of metallic and ceramic tools[18,19.] Metals can be covered with lubricants which lower resistance to motion and slow wearing of surfaces. When lubricants are used on a polymer surface, they cause swelling and *worsening* of tribological properties. Insufficient knowledge of polymeric materials tribology is illustrated by the fact that the fundamental texts that talk about status of polymer science and engineering deal little[12] or not at all[13] with tribology.

In a book on tribology we find friction values but almost nothing else[14]. Development of tribology of PBMs is related to their dependence of properties on the load duration – an effect much smaller for metals and virtually negligible for ceramics[6]. Polymeric materials are *viscoelastic* and their properties *change with time*. Since macroscopic properties of polymers depend on molecular structure and interactions, one expects some correlation between tribological and mechanical properties.

Polymeric materials are used as tribological materials pure, as composites with a filler, as coatings or else as solid lubricants[15]. Thin polymer film monolayers that are created by chemisorption or physical adsorption of organic polymer molecules represent promising surface lubricants in areas that are now rapidly developing, for example memory storage devices, micromechanical systems and other high precision devices[16,17]. Polymers often have complex multiphase structures – what makes evaluation of their tribological behavior relatively difficult[13].

Polymer complex structure and behavior can be analyzed by computer simulations. The key benefit of materials computer simulation is the fact that it can provide information that cannot be experimentally determined, continuous dependence of scratch depth on time among them[10]. Creating polymer structures[11] is much more complex than the creation of metal structure because the polymers consist of macromolecular chains that vary in length, orientation and composition, all of which affect tribological as well as other properties of polymers[12].

2. TRIBOLOGY BASICS

We have defined the main constituents of tribology in Section 1. Sometimes lubrication is also considered as a constituent of tribology since it affects friction and wear. We now begin with friction. It can be defined as the tangential resistance force (F) in the relative motion of two surfaces in contact[2-4]:

$$F = \mu N \tag{1}$$

where N is the normal force and μ represents friction. Eq. (1) has been formulated by Amonton already in 1699. Thus, friction represents the tangential drag force acting in direction directly opposite to the direction of motion. According to Eq. (1), the friction resistance is proportional to the load and μ is independent of the apparent area of contact between the bodies. Much more accurate equipment that we have in our disposal now in the XXIst century show that the Amonton law is approximately obeyed. The parameter μ is often called "friction coefficient"; however, Lord Kelvin himself pointed out that the word "coefficient" provides no information.

The value of μ in Eq. (1) depends on whether the motion has just started or is it already ongoing. In the former case we are dealing with *static friction* $\mu_s = F/N$. With the specimen in motion, *dynamic friction*, also called *kinematic friction*, represents the ratio of force needed to maintain motion at a defined speed and force applied: $\mu_d = F/N$.

Static as well as dynamic friction depend on the interface of the pair of materials in contact, preparation of surface, and interaction of surfaces such as chemical or other reaction of reactive compounds, lubricants, humidity, pollution - all of which may change chemistry and surface topography, and thus significantly affect friction. Contact surface of pure metals and alloys have a strong adhesion due to strong metallic bonds and the corresponding high friction (static friction of about 2 or more) and high wear. Metal oxides and impurities lower the adhesion and thus reduce friction. Ceramics are used in extreme conditions due to their high mechanical strength and resistance due to the presence of strong covalent and ionic bonds, low plastic flow at room temperature. They show generally lower friction values than metals. Polymers, generally with low stiffness and low strength, exhibit low friction given weaker interactions, but high wear in comparison with ceramics and metals. That is the reason for the need of using polymer composites, which ensure a balance between good mechanical strength, low friction and low wear. Lubricants used in the form of solids or films, dry powder or oil (suspension or dispersion) generally reduce friction by creating a thin, low shear strength film on the surface. Application of lubricants ensures reduction of friction, protection against wear and grooving - but only for metals and ceramics. As already noted, polymers in contact with liquid lubricants *swell*. The interactions that occur at the interface determine friction, wear and lubrication - and affect bulk properties also because of transfer of mechanical energy. Physical and chemical nature of the interacting materials surfaces and the surface topography might change.

Sometimes it is mistakenly assumed that interfaces with high friction show a high rate of wear. This is not generally true; both friction and wear have to be determined. There are cases when solid interfaces of polymers show relatively low friction but fairly high wear, while ceramic surfaces show moderate friction but very low wear.

Wear of a material can be mechanical and/or chemical; it is generally accelerated by heating during friction. Wear mechanism can be adhesion, abrasion, fatigue, and the effect of erosion, chemical reactions including corrosion, or else an induced electric arc. Fairly often there is no single mechanism of wear, but a combination of several mechanisms.

3. FRICTION OF POLYMERIC MATERIALS

We have already noted that methods of mitigating wear such as the use of external lubricants cannot be transferred from metals to ceramics. Our understanding of mechanisms of tribological phenomena *also cannot be transferred* from metals to polymers. Mechanical properties of polymers are directly affected by entanglements of polymer chains[20]. The same applies to tribological properties[21]. Therefore, it is expected that specific chemical structures affect tribological properties of PBMs.

In investigating friction, adhesion and deformation are important[15]. Such an approach pertains to all materials including polymers[22,23]. Adhesion component of friction is controlled by creation and breaking of bonds between the actual points of contact on the surfaces. For most polymers, van der Waals dispersive interactions and hydrogen bonds are typically present[24].

Shearing of asperities during movement of partner surfaces results in breaking interfacial bonds. Consider as a reference a fully planar surface without asperities. Any roughness on such a surface means formation of asperities or 'bumps'. The presence of bumps means, first of all, that the effective contact area of the two interacting surfaces is *much* smaller than the nominal area corresponding to fully planar surfaces. This results in a dramatic lowering of friction[25]. The explanation just provided of this phenomenon has been called the bump model[25].

Generally, the interfacial bonds, i.e. their creation, growth and termination are under the influence of the nature of contact areas, surface chemistry, and stress in the surface layers at the given load conditions. Harder particles or asperities are cutting or plowing the surface. If those cutting points are embedded in the counterface, one talks about two-body abrasion. If the cutting points are loose within the contact zone, such a situation is usually called three-body abrasion[26,15]. Deformation component of polymer friction, as a second source of friction with adhesion component, is attributed to the deformation occurring in asperities of the two sliding surfaces. On the point of contact surface, an elastic, plastic and/or viscoelastic deformation takes place. Deformation is accompanied by the dissipation of mechanical energy that depends on the type of strain, conditions of sliding, mechanical properties, environmental and other factors. Factors that influence the tribological properties of polymers are structure and position of macromolecules on the surface, degree of crystallinity, type of polymer (homopolymer, block copolymers, etc.), composition of polymer blends, chain orientation obtained during the processing (extrusion, etc.), molecular structure (linear, branched or crosslinked), and molecular weight distribution. As already noted, polymers are viscoelastic. They are sensitive to heat created during movement since mechanical energy is significantly converted into heat[16.] Heat formation appears during plastic deformation, hysteresis, dispersion and viscous flow. Other heat sources can be attributed to the creation and termination of the adhesive bonds. The basic friction mechanism of polymers in the viscoelastic state across smooth surfaces is adhesion[16]. There is also deformation of the polymer surface layers. These relations were observed for amorphous polymers and rubber products, but are also similar for semicrystalline polymers[26].

The field of tribology has a relatively small number of standards. In the tests, it is important that all test bodies have the same thermal history and the same corresponding conditioning - to eliminate effects of humidity and other environmental factors. According to a standard for friction determination[27], we use a device for measuring the force needed to slide the upper partner over a defined surface of the lower partner; see Figure 1 and again Eq. (1).

An example of dynamic friction results is shown in Figure 2. We find that it is possible to reduce the friction of a commercial epoxy by adding small amounts of fluorinated poly(aryl ether ketone) (12F-PEK). Apparently at a low cure temperature (24°C) the fluoropolymer migrates to the surface[28,29]. That migration lowers the surface tension and changes the surface morphology[28]. By contrast, during rapid curing at a higher temperature (70 °C), the migration of fluoropolymer to the surface is only partial - what leads to increased friction[28]. Instead of bumps of 12F-PEK which lower the contact area, we then have only perturbation of a large contact area of the epoxy and thus higher friction.

The above example shows that the tribological friction properties depend on the composition of polymer blends, thermal history, cure temperature - all of which cause changes on the surface of the sample, and thus change the tribological properties.

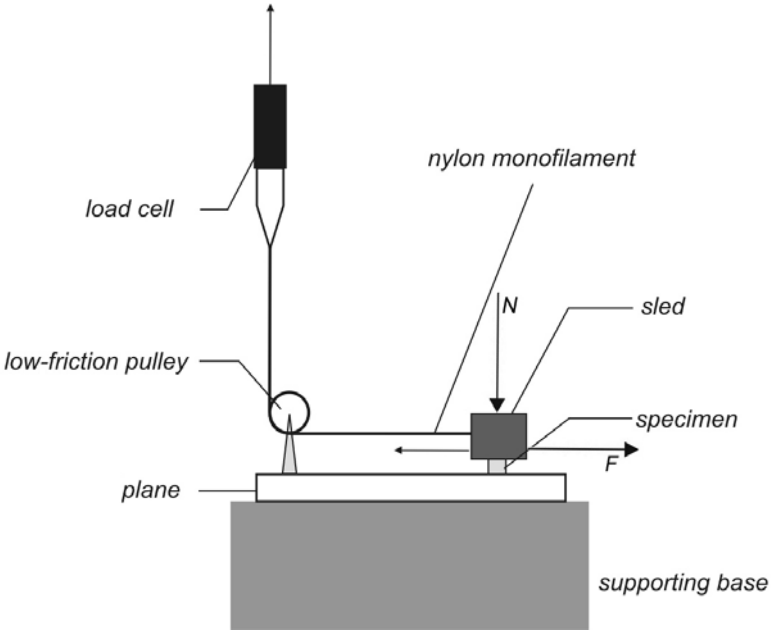

Figure 1. Specimen fixed on the back of the sled slides over the surface of the lower or substrate component creating friction resistance.

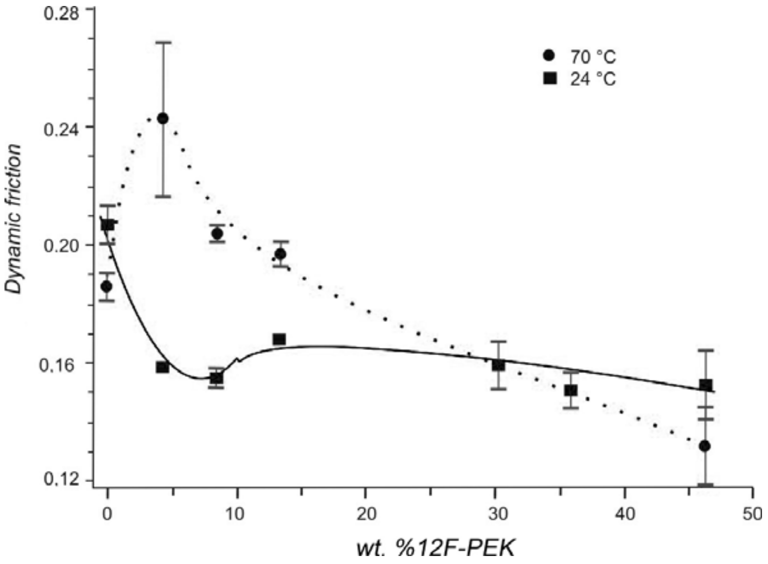

Figure 2. Changes of dynamic friction with composition of polymer blends of an epoxy + 12F-PEK at two curing temperatures (24°C; 70°C); after Ref. 28.

4. SCRATCH RESISTANCE OF POLYMERIC MATERIALS

Scratch resistance is one of the most important parameters determining durability of surfaces. A test method for scratching resistance determination, originally designed to measure the adhesion of thin hard films[30,31], was adapted for the purpose[32]. Generally, the method is based on deformation of surface caused by a moving indenter (stylus) under a load[1]. One measures the depth of grooves or indentations during scratching. In our own work, we use a Micro Scratch Tester from CSM Instruments such as shown in Fig. 3 and equipped with an acoustic signal detection[1,33]. That signal changes significantly if a new phase is encountered by the indenter.

Tests provide the instantaneous or penetration depth R_p and the residual depth after recovery or healing R_h. Because of viscoelasticity, healing is significant, although metals also show some but not large recovery[34]. The recovery amount ΔR is clearly[29,35]:

$$\Delta R = R_p - R_h \qquad (2)$$

The percentage recovery f is calculated from ΔR as[29,35]:

$$f = [\Delta R \cdot 100\%] / R_p \qquad (3)$$

A tester that provides such results[29,33,35] is presented schematically in Figure 3.

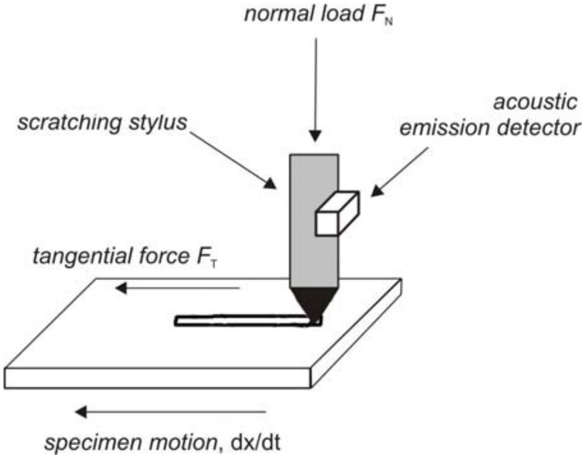

Figure 3. Micro-scratch tester.

We return now to the example of a commercial epoxy + 12F-PEK fluoropolymer. We have seen friction results for it in Figure 2. We now

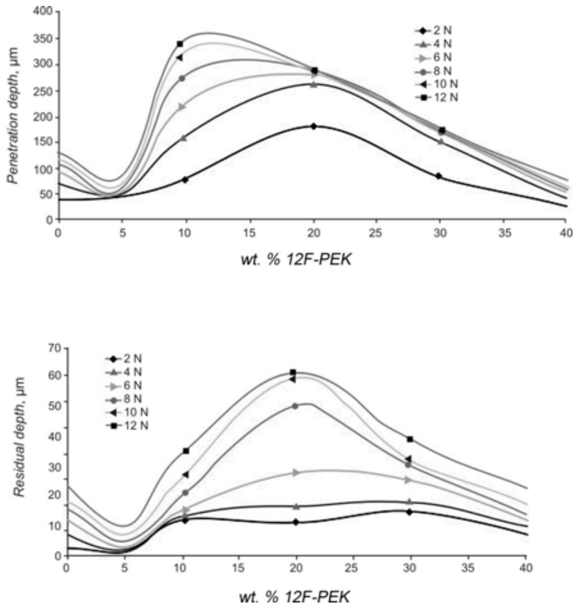

Figure 4. Penetration depth and residual (recovery) depth for several applied forces (2, 4, 6, 8, 10 and 12 N) as function of fluoropolymer (12F-PEK) concentration in blends with a commercial epoxy at the curing temperature 24°C; after Ref. 29.

show R_p and R_h results for the same system in Figure 4. Thus, it is possible to achieve both lower friction and a higher scratch resistance at a low concentration of fluoropolymer – but at a low curing temperature[1,33].

5. SURFACE ENERGY AND TRIBOLOGY

When we change the composition of a polymer's materials at its surface, the surface energy is altered, too. We continue with the epoxy + 12F-PEK example. Surface tension γ has been calculated on the basis of measurement of contact angles[36] for three selected test liquids, two of them polar. It turned out that there is a correlation between γ and tribological properties: R_p, R_h, as well as static and dynamic friction[37]. We see in Figure 5 that the minimum of surface tension and maximum improvement of tribological properties occur at the same concentration of the fluoropolymer in the epoxy[33]. We have sought a relationship between the surface tension and tribological properties because all pertain to the surface phenomena.

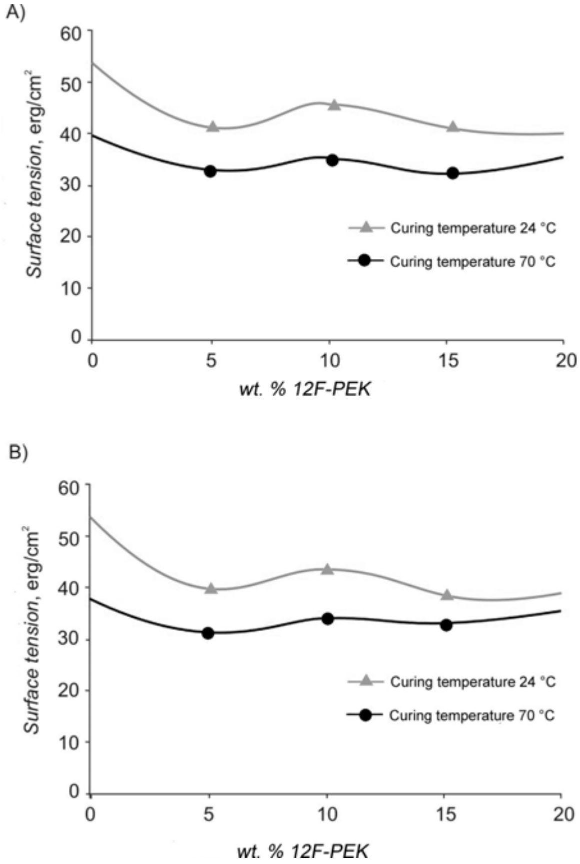

Figure 5. Surface tension as function of epoxy + fluoropolymer (12F-PEK) composition at two curing temperatures (24°C and 70°C) determined by contact angle measured for the top (A) and the bottom of the specimen (B) (after Ref. 37). Three liquids, two polar and one nonpolar, have been used in contact angle measurements.

Many other examples show that changes in interfacial energy markedly affect the properties of multiphase polymer systems. Such systems usually have to be made compatible because of their immiscibility[37-41]. The investigations of compatibilization of immiscible polyurethane and poly(vinyl acetate) blends by addition of a nanofiller[42] were also focused on reduction of interfacial energy and achieving an optimal interface when nanofiller was placed at the interface between the polymers. By continuation of the interface research[43,44] the changes in tribological properties and in particular their relationship with the changes in the interfacial energy of polymer blends filled with surface-treated nanofillers can be followed. The environment such as the level of humidity has to be taken into account.

6. WEAR OF POLYMERIC MATERIALS

One often distinguishes four types of wear: abrasive, adhesive, fatigue wear and wear due to the chemical changes in the boundary layer (tribochemical wear). For polymers, abrasive wear is particularly interesting. As already noted, the basis of abrasive wear is the cutting and plowing of the surface by harder particles or asperities on the surface[15]. Lancaster and Ratner have concluded[45] that for polymers abrasive wear is proportional to $1/(\sigma_b \cdot \varepsilon_b)$, where σ_b and ε_b are the stress and strain at break, respectively. They have also claimed that friction increases along with the increasing ratio $1/(\sigma_b \cdot \varepsilon_b)$, depending on the type of polymer: from low density polyethylene (LDPE) via polyamide (PA66), polytetrafluoroethylene (Teflon, PTFE), polypropylene (PP), polyoxymethylene (POM), to high friction poly(methyl methacrylate) (PMMA) and polystyrene (PS). We have already noted that friction and wear are not necessarily proportional to one another. Interesting, however, is that Lancaster and Ratner talk about inverse proportionality between wear and the strain at break and also between friction and the strain at break. Brittleness of materials – to be discussed more in detail below – is inversely proportional to the strain at break.

The main wear mechanism is adhesion, which is an important component of friction. Adhesive wear process involves creation of adhesive bonds, their growth and breaking when the material is transferred from one surface to another[15]. It is important to note that wear is usually not the result of a single mechanism but a combination of different mechanisms.

Wear is most often defined as the unwanted loss of solid material from the solid surface caused by mechanical interactions[3]. Then wear is quantified by determination of the specific rate of wear μ_{sp} by measuring the volumetric loss of the sample V_{loss} with the applied force F and the length of sliding (D)[1]:

$$\mu_{sp} = V_{loss}/(F \cdot D) \tag{4}$$

According to Eq. (4), wear is determined from the volume (or mass) of fragments, or wear products that are separated from the specimen during the wear. However, the above method (ASTM G 65-85) cannot give reliable results because the amount of debris depends on the relative speed of two surfaces in contact. As already mentioned, a part of the motion energy turns into the heat. With higher speeds more heat is produced, and the experiments are not isothermal[1]. Needless to say, the test temperature has a direct impact on the wear of polymers.

In accordance with the specific heat capacity of the tested couple, the same relative velocity will result in different increase of temperature with different polymers. Therefore, even with fixed velocity during the tests, the results may be meaningless. During the tests some polymers anneal above their glass transition temperature T_g, while others remain below T_g. Therefore, a comparison between mass of products produced during the wear testing has limited value and currently there is no generally accepted test method for determining wear of polymers[1]. We need to note that the apparent *absence* of mass loss in many polymers also makes that particular ASTM protocol unusable – particularly for soft materials that are known to form little or no debris.

7. SLIDING WEAR DETERMINED BY MULTIPLE SCRATCHING

Multiple scratching along the same groove (see again Fig. 3) provides the possibility of determining the sliding wear of polymers. It is a much more reliable method in comparison to determining the abrasive wear - while the results are not equivalent[6]. By determination of wear during the sliding friction, two properties are determined, similarly as in single scratch resistance determination, namely R_p and R_h. A phenomenon of strain hardening during the sliding wear was discovered in 2004 for a polyester[46]. It has been shown that after an

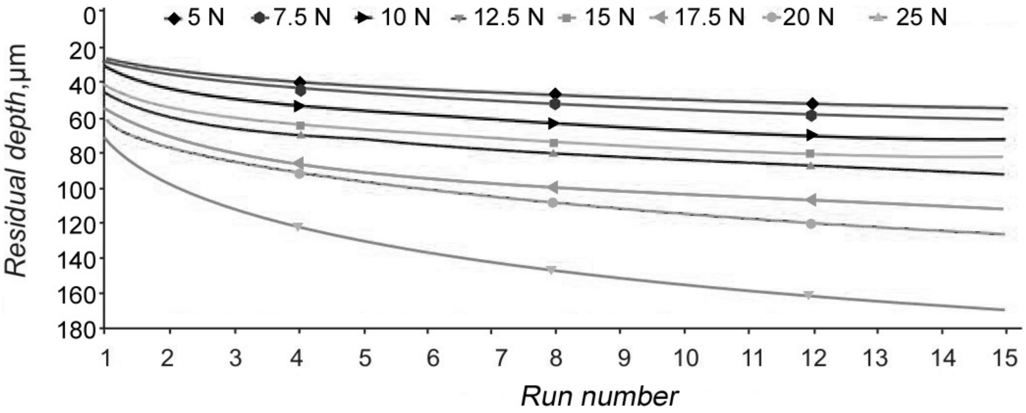

Figure 6. Sliding wear determination for a polyester: residual scratching depth R_h as a function of the run number at several constant force levels; after Ref. 46.

initial increase of the residual scratching depth with the increased scratch number, the material reaches a constant residual scratching depth (Figure 6)[33,46]. In other words, further runs provide no change in depth. The phenomenon has been explained by densification of the bottom and sides of the groove during consecutive runs[47,48]. One of the results of densification is lower nanoindentation depth inside the groove than on the flat surface outside. Again, typically there is little if any debris.

Figure 6 shows that multiple scratching gradually increases residual depth - but only down to a certain limit. Therefore, a new definition of wear is proposed, where a measure of wear $W(F)$ is defined for a given geometry of the test indenter, test speed and force F at 25°C or at some other temperature[1]:

$$W(F) = \lim_{n\to\infty} R_{\mathrm{h}}(F) \tag{5}$$

where n = scratch number.

In practice, multiple scratching experiments should be terminated (Fig. 6) when there is no change in depth. End of test is defined as the value of $[R_h(n + 1) - R_h(n)]/ Rh\ (n)$ is less than 1 % (typically after about 15 scratches)[46]. If there is an asymptote for large forces, the final amount of wear W is independent of the number of scratches and force:

$$W = \lim_{n\to\infty} W(F) \tag{6}$$

The example of results of asymptotic residual depth, R_h, after multiple-scratching under the same force, which is 88 µm for PTFE compared with 43 µm for PP, illustrates the differences in tribological properties and low resistance of PTFE to wear[1]. In practice it has been shown that the PTFE is a material for pans with a corresponding low friction, but it is characterized by very low resistance to scratching and therefore shows a large residual depth after multiple-scratching. Correlation between the results of hardness and surface wear testing of polymers is very questionable due to differences between tests[49]. The results may show that harder material shows less wear, as expected, but also cases where the reverse occurs are known[1].

A notable widely used polymer that does not exhibit this kind of behavior is polystyrene (PS)[6] – a fact associated with its brittleness and discussed below in Section 9.

8. CONNECTIONS BETWEEN DIFFERENT KINDS OF PROPERTIES

It is well known that all macroscopic properties of polymers depend on micro-nano structure and interactions at the molecular level. This suggests the existence of connections between various macroscopic properties[6]. As an example of such behavior is the effect of carbon black as a filler on polymer blends; at a single carbon black concentration there is a rapid descent of the electrical resistance (called the percolation threshold) as well as a rapid descent of the static friction[50]. Near continuity of the carbon black particles that produces a drop in electric resistivity also produces a surface such that in friction determination the sled moves over a much smaller contact surface. That surface consists to a significant extent of carbon black particles.

9. BRITTLENESS

Viscoelasticity of PBMs seems to be a leitmotiv of this article. We have seen above how viscoelasticity results in groove healing after scratch testing. In the present Section we shall discuss first quantitative determination of viscoelasticity. This will lead us eventually to a quantitative definition of brittleness.

Viscoelasticity of PBMs is most often characterized by dynamic mechanical analysis (DMA)[51,52]. The key quantity is the complex modulus E^* which connects the storage (solid-like) modulus E' and the loss (liquid-like) modulus E'':

$$E^* = E' + iE'' \qquad \text{where } i = (-1)^{1/2}. \qquad (7)$$

We now temporarily return to sliding wear determination results. We show respective diagrams for four polymers in Figure 7:

We see in Figure 7 that other polymers show strain hardening in sliding wear but polystyrene does not. Trying to explain this result, we have asked colleagues around the world for their input. A typical response was: "this is not surprising since PS is brittle". Following this line, we have asked in turn what "brittle" means. It turned out that there was no quantitative definition. We have therefore developed one[6,35,53]. At any given temperature T

$$B = 1 / (\varepsilon_b \cdot E') \qquad (8)$$

the strain at break ε_b already seen above can be determined in quasi-static tensile testing while the storage modulus E' from DMA corresponds to the frequency 1.0 Hz.

A definition has to be useful. Since the original reason for developing it was the odd behavior of polystyrene in sliding wear determination, we have studied a connection between B and sliding wear results. Recall now the definition of viscoelastic recovery f by Eq. (3); it pertains to single scratch testing as well as to sliding

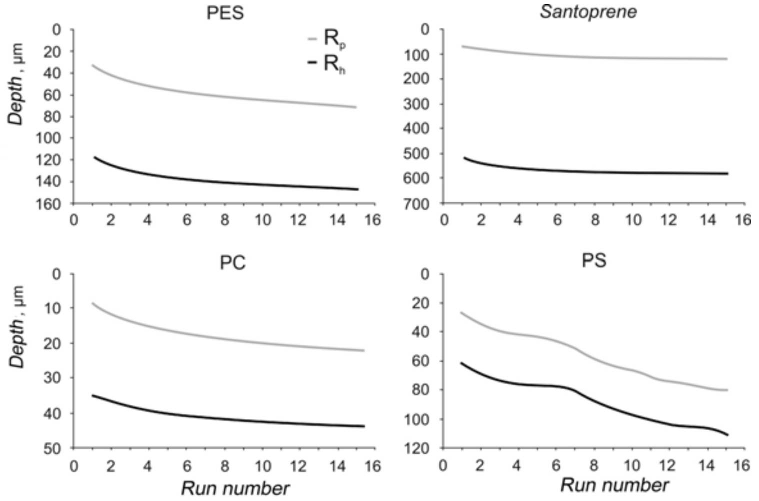

Figure 7. Penetration depth R_p and residual depth R_h as function of the number of scratching runs performed in sliding wear determination for selected polymers: polyethersulfone (PES), polycarbonate (PC), Santoprene™ (an elastomer) and polystyrene (PS).

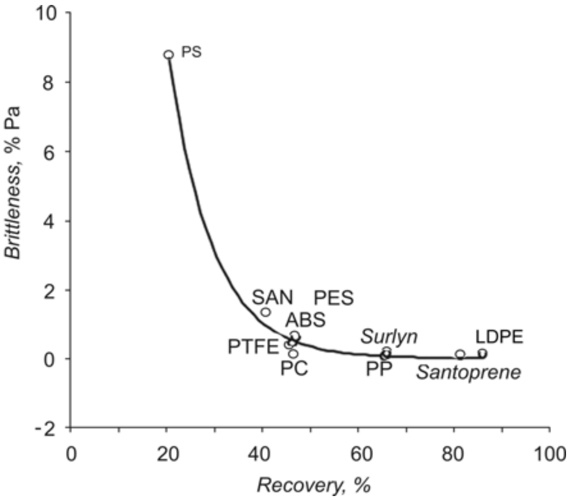

Figure 8. Brittleness as function of viscoelastic recovery for a large variety of polymers. Materials are: polycarbonate (PC); polypropylene (PP); polystyrene (PS); polytetrafluoroethylene (PTFE); styrene/acrylonitrile copolymer [Luran®] (SAN); Santoprene™ (an elastomer); acrylonitrile/butadiene/styrene (ABS); Surlyn® 8149 [ethylene/methacrylic acid copolymer]; polyether sulfone (PES); low-density polyethylene (LDPE).

wear. We have found that there is a relation between B and f in sliding wear valid for all polymers we have investigated[6] (Figure 8):

Polystyrene behavior, which is different from other polymers, can now be quantitatively explained as a consequence of very high brittleness value namely $B = 8.78$ [6]. This is the reason why PS does not show strain hardening in sliding wear. Other polymers shown have much lower brittleness values ($B = 0.09$ for Santoprene; 0.11 for PC; 0.63 for PES[6], as well as $B = 1.35$ for PMMA, 0.19 for PVDF and 1.30 for PPSU)[35]. The definition Eq. (8) has been used also for metals[34] and for composites[53]. Significant differences in B values have been found for two copper pastes with different microstructures[34].

10. STRAIN HARDENING AND FREE VOLUME OF POLYMERS

Recovery after the scratching of polymer surface, which takes place over time, can be associated with general time dependence of mechanical properties of PBMs, as seen for example in creep. Prediction of the long-term behavior of polymers as a consequence of some phenomena such as creep can be achieved by short-term investigations that are based on the determination of free volume of polymers[6]. It can be expected that materials that have more free volume will exhibit a larger recovery *f* in sliding wear. Figure 9 shows the dependence of recovery for various polymers on free volume[6]. Free volume is defined as

$$v^f = v - v^* \qquad (9)$$

where all quantities are specific ones pertaining to a unit of mass such as 1 g; v* is the hard-core volume (corresponding to squeezing out all free space at 0 K and an infinitely high pressure). In practice v* is obtained by fitting P-V-T results to a reliable equation of state.

The results in Figure 9 confirm that more free volume results in larger viscoelastic recovery. All investigated polymers show the same behavior, except polystyrene – an outlier here also[54,55]. We recall the effect of styrene units in polyamide polymer blends which provide a good processability in melts, but weak mechanical properties[56] – one more consequence of high brittleness of PS.

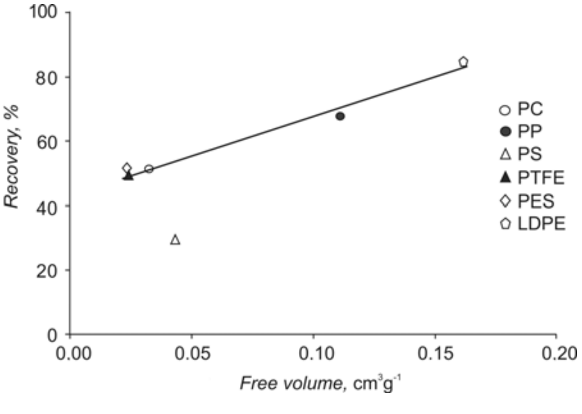

Figure 9. Percentage recovery in sliding wear determination as function of free volume for important engineering polymers.

11. EFFECT OF COMPOSITION ON TRIBOLOGICAL PROPERTIES

Numerous examples illustrate the effect of different additives in polymeric materials on tribological and other properties - depending on the surface characteristics of additives and the level of interactions with the polymer matrix.

Thus, the friction of polymer blends depends not only on the basic components but also on the compatibilizing agent added. A compatibilizer characterized by high friction, such as styrene/ethylene-block-butadiene styrene (SEBS), added to the PP + PS mixture with a small amount of polystyrene generally increases friction[57]. On the other hand, addition of the same compatibilizer to PP + PS blends with a higher initial concentration of PS and a higher initial friction results in friction lowering[57].

The addition of filler or fibers to a polymer matrix reinforces the material when there is good adhesion between the filler and the matrix. Lower friction factor and wear are also expected – but are not generally guaranteed. For example, the reinforcement of polyether ether ketone (PEEK) with carbon fibers does not result in a decrease of friction while it increases volumetric wear compared to the pure polymer - probably due to low adhesion at interfaces[58].

Other examples, however, show opposite effect of the improved resistance to scratching, e.g. poly(vinylidene fluoride) and high molecular weight polyethylene mixture in the presence of carbon black filler, when a good adhesion is achieved[59]. Also, carbon nanotubes added to polyamide matrix improve the properties such as the increase of the initial decomposition temperature, increase of the tensile strength and modulus of elasticity; tribological properties are improved: reduced penetration depth R_p with increasing concentration of carbon nanotubes[60]. However, too high concentration of the nanofiller obstructs the viscoelastic recovery - so that the residual depth R_h does not decrease but does just the opposite.

12. SURFACE PRE-TREATMENT AND WEAR

Literature suggests several ways how to reduce or eliminate wear by various surface processing and pre-treatment, thereby improving adhesion between matrix and additives (fibers or fillers) in the composites[61].

In epoxy + silica hybrid materials friction and wear are significantly reduced, as a result of silicon dioxide particles which prevent crack formation. On the wear surface of polymer hybrid one can see finer waves compared with those of pure epoxy[62]. Inclusion of silica nanoparticles in polymer latex, especially by in-situ polymerization, markedly improves the resistance to wear, which is particularly important in applying water dispersion coatings where interaction at the interface can be improved by adding more surface active and/or functionalizing agents[63].

Increase of adhesion between reinforcing fibers and the polymer matrix can also be achieved by plasma treatment of carbon fibers[64], or by grafting methyl methacrylate on surfaces of the fibers[65].

In our work, in order to improve adhesion at the interface and mechanical properties of materials, different micro- and nanofillers have been used[42-44]. The results have confirmed highly improved tensile strength and higher glass transition temperature in the case when optimal adhesion on the interface has been achieved. Various modifications of polymer structure[65], such as chemical modification by crosslinking of thermosetting polymers, or addition of fluorinated polymer in the epoxy resin, change the surface properties and thereby change the friction and wear[28,35,67].

An example of polymer liquid crystals (PLCs) surface modification by imposition of magnetic fields provides another option[68]; see Figure 10. Static and dynamic friction factor of the initial PLC sample changes after the action of the magnetic field on the sample with initially relatively small spherical LC islands (Fig. 10 a) and sample with parallel (Figure 10 b) and vertically oriented rigid LC islands (Figure 10 c). The magnetic field creates larger, rigid and oriented LC islands in the PLC (b and c in Figure 10) - what increases resistance to movement.

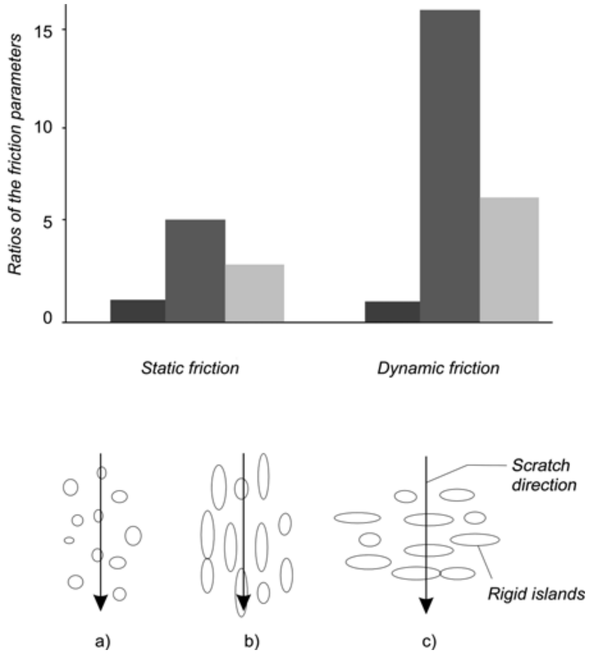

Figure 10. Static and dynamic friction of an initial sample of a PLC (left bars) with relative small spherical LC *islands* (a); under the influence of magnetic field (middle and right bars) depending on the orientation of LC crystals (b, c).

Application of protective coatings such as nanohybrids of the polymer + inorganic filler type increases also the scratch resistance of *teeth*[67]. Scratch testing of bone as a natural nanocomposite that consists of layered hydroxyapatite nanofiller and collagen as organic matrix, as well as by testing the effect on nanohybrid coating on the resistance to scratching illustrates that natural nanocomposites show significant recovery; see again Eq. (2). These results show effects of viscoelasticity of natural nanocomposites on the tribological behavior as similar to that of polymers. Metals show much less recovery[34] while the recovery of ceramics is negligible.

13. COMPUTER SIMULATIONS

The reasons for using computer simulations lies in possibilities to observe and analyze phenomena and processes without the necessity of experimentation, especially for the research of polymers on meso-level, as well as on nanolevel[69]. This way, creation of new materials with new structures, checking hypotheses, models and theories, and quick access to individual test results with variables changed one at a time is possible.

Molecular dynamics (MD) computer simulations give insight into the behavior of polymeric and metallic materials[21,70-73]. The MD method was used in the simulation of mechanical properties of metals and polymers such as tensile properties of polymer liquid crystals[72], and simulation of crack formation and their propagation[73]. In this method an important step is the process of creating the three-dimensional computer model of a polymer, which is based on the results of real materials experiments[19].

Simulation of the scratching phenomenon was conducted using a similar method as the simulation of tensile deformation[21,72]. Only in this case the applied force was perpendicular to the surface of the material and the resulting local deformation was measured. An indenter (dark element in Figure 11) scratches the surface of the polymer chain segments that are shown as spheres[69]. Simulation of scratching provides continuous information of the behavior of each polymer segments in time. A classic experiment gives only two values: the average penetration depth R_p – here the average of bottoms of the curves and the average depth after recovery R_h – in simulations the average of the horizontal asymptotic values.

MD simulations of scratch testing of polymer liquid crystals scratching show that the presence of rigid segments - especially their spatial distribution rather than their concentration - improves the tribological properties namely causes shallower penetration and recovery depths.

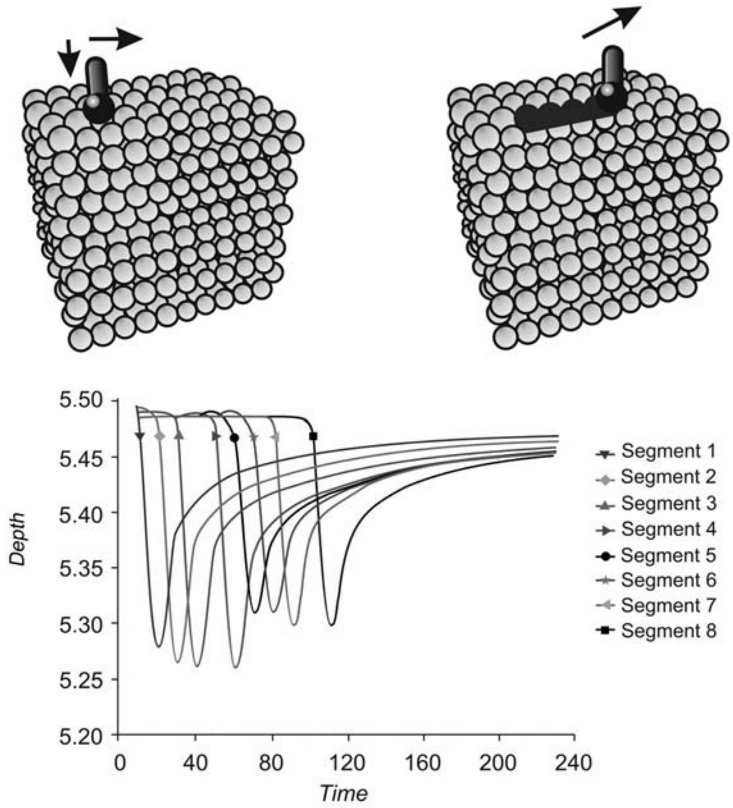

Figure 11. Simulation of scratch testing.

14. MICRO- AND NANO-TRIBOLOGY

Macro to micro-and nano-level analysis provides new insights into materials properties - including the tribological properties. When adhesion is achieved at interfaces at the nano level, improved properties are obtained. Properties of nanohybrids, including tribological properties, of composites obtained by a chemical reaction between inorganic and organic components, or by mixing the components at the nanolevel[67] are substantially different and improved in comparison to *heterogeneous* composites. In the latter the components are mixed at a macroscopic level[75,76].

Useful techniques include scanning tunneling microscopy (STM), which gives three-dimensional image of the solid body's surface. Atomic force microscopy (AFM) with atomic resolution measures ultra small forces (less than 1 mN) that exist between the AFM surface and the surface of specimen. The specimen can be electrically conductive or constitute an insulator. This enables better understanding of interfacial phenomena in small-scale – useful for structures used in magnetic memory systems, micro-electromechanical systems (MEMS) and other industrial applications. The study of micro- and nano-tribology helps in understanding of interfacial phenomena in macrostructure - as a bridge between basic science and engineering. The tribology is not a new science but it is important to develop a specific approach for the polymer-based materials (PBMs) regarding their properties and to disseminate the knowledge about the PBMs tribology[77].

15. CONCLUDING REMARKS

Increasing interest in PBMs and their applications in the industry, as an efficient replacement for metals and other materials, is based on our ability to create and change their structures over a wide range. This enables property improvement - including modification of tribological properties.

The main problem of wider use of PBMs is their strong behavioral dependence on temperature that is reflected in their mechanical properties, as well as their low thermal conductivity, tendency to creep and its sensitivity to environmental effects.

Tribological properties of PBMs depend on their composition, but also depend on the thermal history such as different temperatures of solidification. All these affect the surfaces and thereby tribological properties. Further progress in determination and improvements the tribological properties of polymers and PBMs i.e. their composites and blends is possible by finding links between the friction factors and the wear mechanisms, but also by modification of surface structures at micro- and nano-levels.

New possibilities of application of PBMs depend on the results of further investigation of their mechanical and tribological behavior – given new challenges in science and technology[78]. Characteristics and properties of polymers such as viscoelastic behavior, brittleness, free volume and changes in the structure formed by addition of components or various modifications during processing are important in establishing functional connections with the tribological behavior of PBMs.

Tribological behavior of polymers can be also investigated by computer simulation of structure and its changes, as well as the effects of structure on the tribological properties as a confirmation and/or as the replacement for the experiments.

Surface tension and tribological properties (friction, scratchability and wear) are surface phenomena and their relationships are useful for optimizing desired properties. We have discussed above connections of surface tension (believed to be the domain of physical chemists rather than engineers) to tribological properties. We believe that examples discussed in this article demonstrate the need for sufficient inclusion of polymer tribology into university instruction – as well as for more research in this area.

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