

# Wear of polymers: an essay on fundamental aspects

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This paper reviews fundamental aspects of the wear of organic polymers and represents a personal view of the state of our current understanding of this subject

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*"A wayward, capricious child of mixed and uncertain parentage"*

*Professor D. Tabor speaking on wear in 1967*

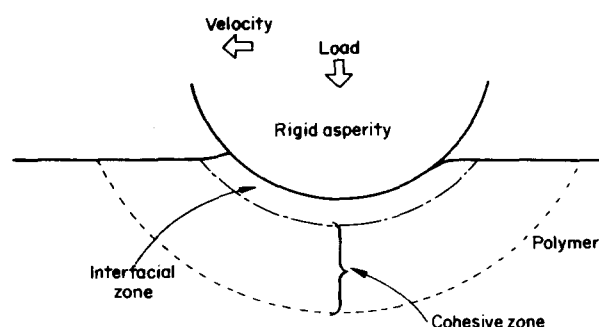
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Much has been written on the wear of polymers, particularly in recent years. Lancaster and more recently Lancaster and Evans have produced comprehensive reviews<sup>1,2</sup>, Tabor and the present author<sup>3-5</sup> have also reviewed certain aspects of the subject and Bartenev and Laurente<sup>6</sup> have published recently a summary of Soviet work. A major compilation has been edited by Lee<sup>7</sup> and various collections of papers have appeared recently<sup>8-11</sup>. In addition many reviews have been published which deal with specific mechanisms or materials; references 12 to 16 are selected examples. A large collection of electron micrographs of polymer surfaces, many of which have been worn, has also been published recently<sup>17</sup>.

This paper is a personal view of our current understanding of this broad topic. Two general classes of wear processes, cohesive wear and interfacial wear, are envisaged and reviewed (Fig 1). Cohesive wear processes include those mechanisms which involve the dissipation of frictional work and its resultant damage in relatively large volumes adjacent to the interface. Abrasion and fatigue wear induced by tractive stresses are within this category. These wear mechanisms are, by and large, controlled by the cohesive strength or toughness of the polymer. The level of deformation or work is a function of the details of the interpenetration of the surface asperities and the magnitude of the surface traction. The proposed mechanisms of these wear processes rely upon an understanding of the mechanical properties of the polymer and invariably the wear rate is correlated with a strength, toughness or fatigue property which is more or less accessible in relatively simple bulk deformation experiments. Sensible correlation of wear data and bulk deformation data does require the definition of the deformation conditions within the contact which represents the major difficulty in this approach. While the details may never be resolved, it appears that for the relatively large volume, approximately isothermal, deformations which occur in cohesive wear processes the extents of and rates of deformation relate to material properties measured in simple deformation experiments.

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This article is based on a paper presented at the 3rd International Conference on the Wear of Materials, San Francisco, 1981, which was published in the Proceedings without figures



*Fig 1 Two general categories of wear processes: interfacial wear and cohesive wear. The sharp distinction between the two regions is artificial but facilitates the subdivision of wear processes into two classes*

The category of interfacial wear processes involves the dissipation of the frictional work in much thinner regions and at greater energy densities. Transfer wear and chemical or corrosive wear are the two elements. The chemistry of the surfaces and the forces emanating from the surfaces are now additional considerations although the mechanical properties also play an important role. The mechanical properties correspond to significantly higher rates and extents of deformation and have no obvious precedence in bulk deformation experiments. These narrow surface regions suffer overall and transient temperature rises of uncertain extent and duration.

The classification scheme outlined above has been adopted elsewhere but with rather different semantics. Lancaster has offered a more detailed subdivision. These classification systems have the virtue that they provide a substantial and useful simplification of a complex problem. In practice, however, wear processes are not monomechanistic and even simple model wear experiments involve a number of rather ill-defined and interacting processes. Without this classification and the implied assumption of separate non-interacting mechanisms an intractable subject would become unassailable.

## Cohesive wear

The general feature of cohesive wear processes is that they are governed, in a large part, by the cohesive strength of the polymer. The frictional work is dissipated within a relatively thick surface zone either through the interaction of surface forces and the resultant tractive stresses or simply via geometrical interlocking of interpenetrating contacts. The extent of this surface zone is defined by the geometry of the contact and the contact stresses generated in the surface. Typically these zones will be of a thickness which is of the order of a contact length. A contact between

rough surfaces will have a relatively small contact length of perhaps a few microns associated with the discrete asperity contacts and a longer length defined by the apparent area of contact. The definition of the apparent contact length is problematic; a circular contact area in linear motion has contact lengths ranging from zero to the contact diameter. The analogous quantity in a thrust washer configuration defies simple description. The deformation processes thus operate within the bulk of the polymer and the damage generated will be a characteristic of the bulk polymer. Such factors as gradients in chemical constitution or molecular organisation close to the surface will not be major complications save in those cases where incipient surface flaws play a major role in the damage process. Such flaws are of importance in brittle solids and may exert the same influence in certain organic polymers.

The notion of mechanical damage induced within the interior of the polymer surface under relatively mild conditions is consistent with the general correlation which has been observed by several workers between wear rate and a measure of the reciprocal of the work to rupture of the same polymer (Fig 2). This type of correlation was initially adopted in an extensive way by Ratner and his associates<sup>18,19</sup> and has been critically reviewed and extended by Lancaster<sup>1,20,21</sup>. Eiss and Warren<sup>22</sup> have recently described the same correlation in some detail for polychlorotrifluoroethylene (pctfe), polyvinyl chloride (pvc) and nylon 6:6. These data were generated by measuring the 'single pass' mass loss per unit sliding distance when a slab of polymer is drawn slowly over the surface of rigid roughened counterface (Ratner preferred gauzes) under a fixed load. Although a 'single pass' may involve numerous asperity interactions within a given area of the polymer surface and indeed progressive changes in the effective surface topography from the front of the polymer to its rear as debris accumulates in the troughs of the roughness, the overall surface topography is essentially unchanged. The bulk parameter used in many early correlations is the reciprocal of the product of the rupture stress,  $\rho_y$ , and the associated strain,  $\epsilon_y$ , as estimated in conventional failure tests in tension on shaped or notch specimens at relatively low rates of imposed strain, ca  $10^{-4} \text{ s}^{-1}$ . It is reasonable to assume that the product  $\rho_y \epsilon_y$  is roughly proportional to the work required to rupture in this configuration and indeed it is unlikely that such an assumption would lead to an error of more than a factor of two over the various types of possible deformation behaviour prior to failure. Warren and Eiss used the actual value of the work to tensile rupture.

The approximately linear relationship between single pass abrasive wear on a given counterface and the reciprocal of the work to rupture ranges over rather more than two orders of magnitude for the twenty or so semicrystalline and glassy polymers studied by various authors. In the worst cases, for example, polyphenylene oxide and nylon 6:6 the deviation is no more than a factor of five from the mean. Typical data for elastomers also fit reasonably well on to the common dependence.

Several doubts surround the value of this useful correlation and emphasise the intrinsic uncertainty regarding the nature of the deformation processes within the contact. There is a general belief that the simple low strain rate tensile test cannot sense the appropriate strength or toughness property of the polymeric matrix. For example, the rate of strain may be too low and the geometry of the

stress system unrealistic. More seriously the damage process is likely to be of a fatigue rather than a unitary nature. Oberst<sup>23</sup> has discussed the apparent strain rate disparity and suggested that the localised shear bands or deformation zones which proceed a crack in a bulk test could perhaps correspond to the local values of the rates of deformation in the contact. In any event there is an indication that many polymers do not show substantial increases in  $\sigma_y \epsilon_y$  with rates of strain<sup>24,25</sup> and adiabatic heating effects would compensate for the inherent viscoelastic character<sup>26</sup>. The difference in stress states and the uncertainty regarding the importance of cyclic deformation remain largely unresolved.

Fundamental studies which seek to answer some of these questions are of two kinds. Model experiments which attempt to study the damage created by single asperity contacts in which the wear rate itself is not monitored, and, secondly, where the wear measurements themselves are carried out upon rough surfaces. In the latter experiments the careful characterisation of surface topography is of major importance but unfortunately few studies have attempted to properly quantify this variable. These two types of experiments are now reviewed separately for the three broad groups of polymers: elastomeric, glassy and ductile.

### Elastomers

*Single contacts* Schallamach<sup>13,26</sup> has studied the damage produced by relatively large rigid indentors when they are drawn over the surface of an elastomer. The damage produced by these 'isolated stress concentrations' was of two forms depending upon the radius of curvature of the indentor. With a sharp gramophone needle, which penetrates deeply into the rubber, the surface damage is in the form of more or less periodic tears in the direction of motion. Schallamach described their formation as follows. The needle stretches the surface layers of the rubber at the rear of the contact and also pushes forward a prow of rubber. Large elastic strains are produced and the rubber ruptures in a direction transverse to the sliding direction. When the surface relaxes these flaws then rotate through almost  $\pi/2$  and produce the observed damage. The sliding

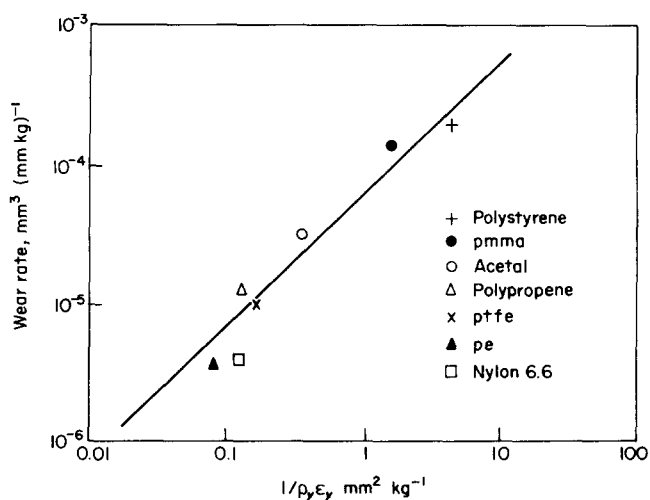


Fig 2 The Ratner-Lancaster correlation of 'single-pass' wear rate against the product of the reciprocal of the stress and strain at tensile rupture. The correlation is remarkably good and emphasises the tensile nature of the abrasive rupture. Counterface roughness ca  $1.2 \mu\text{m } R_a$ . Data mainly from Lancaster<sup>2</sup>

motion is intermittent and characteristic stick-slip behaviour is noted in the sliding force. If it is assumed that each cycle in the stick slip motion corresponds to a tear formation, the work required to form the tear in the surface may be estimated. Schallamach's data are consistent with there being less apparent damage with tougher or higher tear resistant rubbers judged from this frictional work and bulk tear tests. This process does not produce wear debris *per se* but the prow lip of rubber may become detached as the needle releases itself from its elastic restraint (Fig 3).

Experiments with relatively blunt indentors or at lower loads produce a characteristically different type of tear of general importance. Surface tractions are now responsible for much more gentle tensile stresses at the rear of the contact. The damage is in the form of crescents arranged with their concave surfaces facing the direction of motion. The action of the stress also appears to lift or 'tease up' a lip of rubber ahead of the tear.

These single contact experiments indicate the importance of a number of variables in the damage process and establish the role of toughness and the tensile nature of the failure process. These studies are very useful in this sense but they do not specify how material is ultimately detached nor emphasise what is believed to be the essentially fatigue nature of the wear process in many cases.

**Multiple contact studies** These studies are devoted to measuring the abrasion resistance when a rubber is slid over a rough surface. The wear behaviour of elastomers is complicated somewhat by the generation of characteristic surface features or 'abrasion patterns'. Schallamach<sup>13</sup> has reviewed this subject. Unidirectional abrasion produces striations transverse to the sliding direction and the resultant surface topography resembles that of saw teeth with the 'cutting direction' of the 'saw' in the opposite direction to that of the abrasion. The wear which results from this type of process produces relatively large debris and the overall rate of wear is perhaps 50% greater than for abrasion where the direction of motion is altered periodically. The latter was termed 'intrinsic abrasion' by Schallamach and the wear debris is of a smaller scale. Unidirectional abrasion is technically of more importance and the qualitative difference between the two processes has been suggested to arise from what have been termed 'undercutting' effects. When abrasion patterns form the 'saw teeth' are pulled over by the asperities and the resulting lip of rubber is gradually pulled away. Similar types of patterns have been reported by Reznikovskii and Brodskii<sup>28</sup> when rubbers are slid against smooth surfaces under high tractions. A characteristic roll of debris is formed. Aharoni<sup>29</sup> has identified similar types of debris with other polymers. The factors influencing the formation of abrasion patterns have been reviewed more recently by Southern and Thomas<sup>30</sup>.

In intrinsic abrasion experiments Schallamach was able to establish a good correlation between the velocity dependence of the abrasion process and the strain rate dependence of the tear strength of the same rubber in a tensile test. In the same study Schallamach concluded that when abrasion patterns were formed the rate of mass loss was probably governed also by the fatigue strength of the rubber. Champ et al<sup>31</sup> have studied this type of process using a model two-dimensional asperity constructed out of a razor blade as the abrasion member in unidirectional

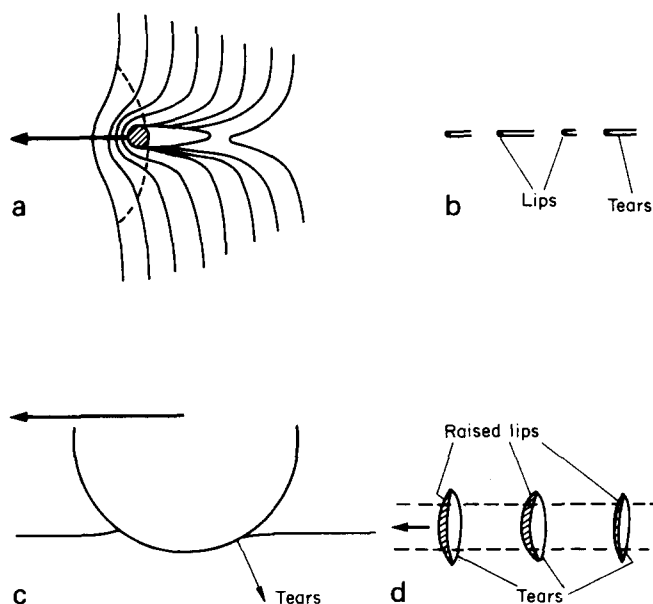


Fig 3 Damage created 'by isolated stress concentrations' on the surface of elastomers. Mainly from Schallamach<sup>13,26</sup>. (a) Sharp gramophone needle. The rubber is pulled forward in the direction of motion and fails in tension behind the contact at  $\pi/2$  to the tensile field. (b) After the needle jumps forward the surface relaxes and tensile tears are evident in the surface but are now in the direction of motion. (c) Tearing of rubber due to tractive stress with a large unlubricated indentor. The tear is generated at the rear of the contact region and is almost at right angles to the sliding motion. (d) A raised tip of rubber is formed but no material is actually removed

abrasion. Their data showed that the velocity dependence of the wear rate was similar to the strain rate dependence of the rate of crack propagation in a bulk 'trouser' test specimen under a cyclic load. The fact that such patterns form is strong evidence for a fatigue process rather than simple unit rupture.

Ratner<sup>18</sup> has summarised the likely contributions from unit and fatigue processes for the range of mechanical responses of organic polymers. Fatigue models for the wear of elastomers have been suggested by numerous authors, particularly from the Soviet Union. Lancaster<sup>1</sup> has reviewed the models in some detail. The work of Kraghelskii and Nepomnyashchii is particularly interesting and established a reasonably good correlation between fatigue life and abrasive wear<sup>32</sup>. Further evidence for the essentially progressive nature of the damage process may be found in the influence of environment and fatigue stabilizers on the abrasion resistance of elastomers. Ratner and Lure<sup>33</sup> and Brodskii and Reznikovskii<sup>34</sup> have studied a range of polymers and concluded that fatigue damage inhibitors effect reduction in abrasive wear under certain circumstances. More recently Gent<sup>35</sup> has shown that the same substances may also reduce the wear of a steel abrasive member by presumably suppressing the concentration of free radicals in the contact zone.

In summary one concludes that elastomeric surfaces are damaged by the creation of cracks orthogonal to the sliding direction in tensile stress fields which probably originate at the surface. The cracks propagate into the bulk of the polymer and ultimately close to form a debris particle. The models developed do not however specify the size of the debris particle; they suppose only

a connection between the rate of fatigue damage and the rate of wear.

### Glassy polymers

**Single contacts** Little work has been carried out with these materials. They are essentially brittle materials in tension but the hydrostatic stresses generated in the contact region will convey significant ductility. The ductile-brittle transition pressure for polymethylmethacrylate (pmma) and polystyrene (ps) at 20°C is ca  $3 \times 10^7$  Pa<sup>36,37</sup>. Significant plastic deformation has been reported for such systems. Puttick et al<sup>38</sup> have recently examined the hardness of pmma and shown that substantial plastic deformation occurs in normal loading. Other subsurface damage is also evident. Nosker<sup>39</sup> has also shown that the time dependent indentation hardness is similar to the scratch hardness on a similar time scale. Our best guidance for the nature of the incipient crack damage during sliding comes from work on organic glasses<sup>40,41</sup>. The damage resembles that described earlier for the case of elastomers under surface traction<sup>37</sup>. Such factors as the relative moduli of the contacting solids and the level of traction are important. The failure characteristics of glassy polymers are also particularly sensitive to the presence of stress crazing and cracking agents<sup>42</sup>.

**Multiple contacts** The Ratner-Lancaster correlation is found to hold quite well for single pass abrasion for pmma and ps below their respective glass transition temperatures<sup>1,20</sup>. Abrasion studies suggest a failure process intermediate between elastomeric and semicrystalline response<sup>42</sup> (see later). Some indication of balance between plastic flow and viscoelastic cracking may be judged from the influence of solvents and surface topography on the rate of abrasive wear.

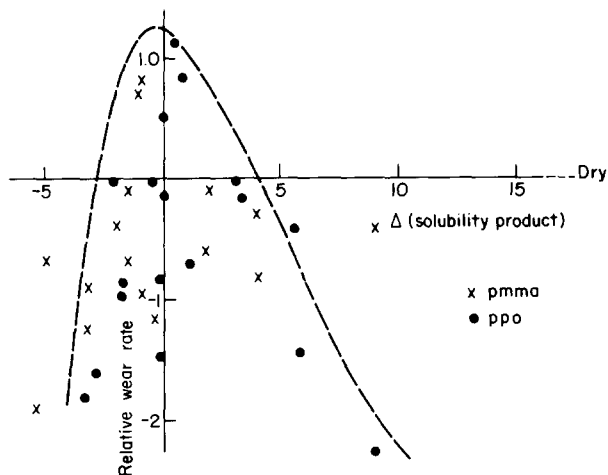


Fig 4 Effect of various fluids on the relative wear rates of polymethylmethacrylate (pmma) and polyphenylene oxide (ppo). The fluid's character is expressed in terms of its solubility product relative to that of the polymer.  $\Delta$  (solubility product) is the difference between the calculated solubility products of the fluid and the polymer and is an inverse measure of the chemical affinity of the two. The wear scale is the logarithm of the wear rate normalised by the dry wear rate. When the fluid has a strong affinity for the polymer, the wear is generally increased. Adapted from Evans and Lancaster<sup>2</sup>. These data indicate that either plasticisation or environmental stress cracking is occurring in the contact region. These types of effects are not evident in more chemically inert and ductile polymers such as ptfe and polyacetal

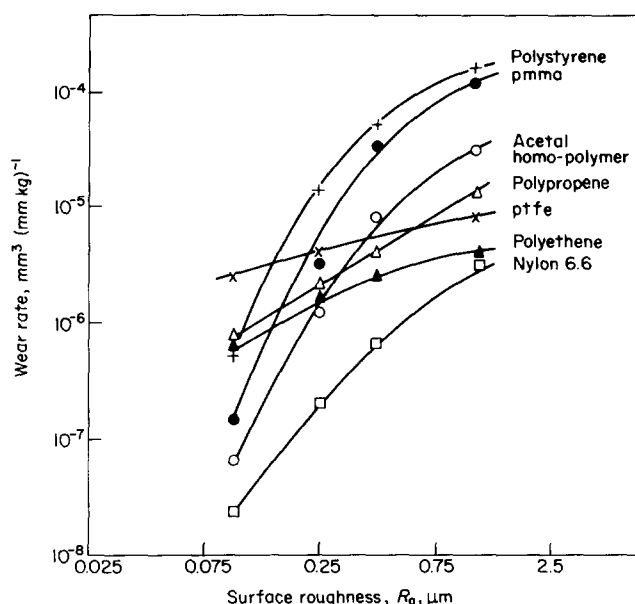


Fig 5 Wear rate as a function of surface roughness for various polymers during 'single pass' abrasion. All polymers showed a marked increase in wear rate as the roughness increases (save for special cases) but the effect with glassy polymers is more pronounced in these experiments<sup>1</sup>

Lancaster and Evans<sup>2,44,45</sup> have made an extensive study of the influence of various solvents on the abrasive wear of a range of polymers under conditions where the load carrying capacity of the fluid is believed to be negligible. The evidence for extensive surface cracks is not evident for pmma in these studies which is consistent with the associated plastic deformation noted in model contacts. Presumably the influence of hydrostatic stress, frictional heating and possibly solvent plasticisation either inhibits or masks the evidence of brittle lesions. The influence of solvents does however indicate an important difference between an essentially ductile polymer such as ptfe and intrinsically brittle polymers, for example, pmma and ps (Fig 4). As the solubility product of the solvent is increased the rate of wear of ptfe on a given surface is relatively unaffected. For pmma and ps a pronounced maximum in the rate of wear is observed when the solubility product of the liquid is close to that calculated for the polymer. It is not clear whether this is due to plasticisation or embrittlement effects although the solvents such as acetone which produce high wear do indeed lead to accelerated stress crazing<sup>42</sup>.

Further evidence for the rather different damage processes in glassy and ductile polymers emerges from study of the influence of surface topography on deformation wear. Such data have been reported by Lancaster and others. As might be anticipated the rougher the surface the greater is the wear. The role of topography of the surface on deformation wear is considered later but for the present it is worth noticing that the wear rate of glassy polymers such as ps and pmma are significantly more sensitive to the roughness variable than more ductile polymers such as pe and ptfe. From Lancaster's<sup>1</sup> survey, the factor seems to be typically of the order of ten (Fig 5). Simple theories of abrasive wear (see later) would suggest that the probability of forming a wear particle per asperity deformation ( $K$  in Eq (4)) is significantly greater for these glassy materials. This may be interpreted as evidence of a unit wear process rather than fatigue. The fact that a material such as pmma can accommodate significantly less strain

before rupture than a ductile material like ptfе may be significant. Alternatively, it may be that the debris fragments are larger for brittle polymers.

A feature of glassy polymers and indeed elastomers is that they do not transfer coherent films of relatively degraded material to counterfaces during sliding. This topic is developed further in the next section. It is however interesting to note that when frictional heating is substantial, the glass transition temperature of the polymer is exceeded and gross surface melting occurs with an accompanying gross transfer of material to the counterface. The rate of wear then shows a substantial increase in magnitude. Molten polymer is then extruded from the rear of the contact and collects at the rear of the specimen in the form of discrete sheets stacked together at an angle inclined to the direction of motion (Fig 6). The influence of ambient temperature, load and sliding velocity have been examined in some detail and are well reported by Lancaster<sup>1</sup> for a range of glassy and ductile polymers. The results are close to what might be expected on the basis of frictional heating calculations and the thermally dependent mechanical properties of the polymers. For example, the wear rate of pmma increases dramatically as the material enters the rubbery state. The transition temperature from low to high wear is probably a little higher than anticipated from studies of the glass transition temperature in conventional tests (frictional heating apart) and may reflect the influence of hydrostatic stress and high rates of deformation in the contact zone.

The damage considered so far is thought to occur at the interface or surface. This is likely to be the case for high tractions. The maximum shear stress appears below the surface in rolling. Archard and Wannop<sup>46</sup> have observed substantial subsurface damage in rolling pmma contacts which are consistent with extensive viscoelastic losses and subsurface heating.

### Ductile polymers

#### Single contacts and a simple model for abrasive wear

The comments made in the context of glassy polymers are appropriate except that brittle or low strain fractures are not evident. The theories of the deformation of ductile solids by rigid indentors are not exact mainly because of the progressive change in geometry during deformation. A simple theory for ductile abrasion is based upon the geometric resistance of a volumeless solid similar in form to that used to model the deformation friction of ductile solids<sup>3</sup>. The approach is useful as it introduces the main system variables. The model asperity is a conical indenter of slope  $\theta$ . The friction coefficient,  $\mu$ , is<sup>47</sup>

$$\mu = 2/\pi \tan \theta \quad (1)$$

This work is dissipated in front of the asperity through a projected area,  $A$ , where

$$A \approx 2W \tan \theta / \pi H \quad (2)$$

$W$  is the normal load and  $H$  is a time dependent hardness. The deformed volume is assumed, on dimensional grounds, to be proportional to  $A^{3/2}$ . The probability of this volume creating a wear particle is ascribed a single value  $K'$  per unit sliding distance. Hence the wear per unit sliding distance produced by this asperity  $z$  is

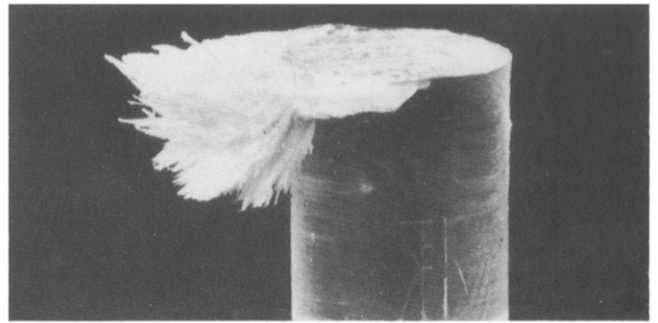


Fig 6 Appearance of a worn sample of pmma where appreciable surface melting has occurred. The pin is about 10mm in diameter and has been sliding at high speeds on 'smooth' steel from left to right. The characteristic tail of extruded material is evident at the rear of the contact

$$z \approx K' \left\{ \frac{2W \tan \theta}{\pi H} \right\}^{2/3} \quad (3)$$

The important variables of hardness, slope and load emerge. For an assembly of abrasive contacts the number of contacts of area  $A$  per unit sliding distance is in proportion to  $A^{-1/2}$  and the total wear per unit sliding distance is of the form

$$z = KW \tan \theta / H \quad (4)$$

$K$  is a new constant, related to  $K'$ , but containing additional terms.  $\theta$  is some mean slope of the effective asperities. Kraghelskii<sup>48</sup> has popularised the use of this type of expression and it is found to be generally applicable within certain limits for ductile metals.

**Multiple asperity contacts** In Eq (4), the constant  $K$  may be reasonably assumed to contain the criterion for damage sensitivity considered earlier: the product of the stress and strain at rupture  $\sigma_y \epsilon_y$ . Ratner et al<sup>19</sup> expressed the function rather differently which may be obtained by including (1) in (4):

$$z = k' \left\{ \frac{\mu W}{H \rho_y \epsilon_y} \right\} \quad (5)$$

$\mu$  is the coefficient of friction at the junction.  $k'$  is again a parameter which describes the probability of forming a debris particle. The hardness will be proportional to the compressive stress  $(\rho_y)_c$  and hence it may be that a material parameter  $\{(\rho_y)_c \rho_y \epsilon_y\}$  is more significant. The Bauschinger effect will ensure that  $(\rho_y)_c > \rho_y$  but the two are related at a given deformation frequency. In the event it appears that it is  $\rho_y \epsilon_y$  (or the actual work to rupture) which is important although the inclusion of a second term in  $(\rho_y)_c$  would probably not significantly change the quality of the correlation.

The relationship between wear rate and the slope of the asperity is evident in the Kraghelskii model and a number of authors have investigated this trend. Early work from Lancaster<sup>1</sup> and others have noted the importance of the mean slope. Before the advent of sophisticated data recovery systems for surface profilometers it was assumed the distribution of asperities heights was Gaussian and that the mean slope was not correlated with height and was also proportional to  $R_a^{1/2}$ . Early data<sup>1</sup> show that this is approximately the case. The data of Hollander and Lancaster<sup>49</sup> involved a more comprehensive topographic analysis and their data indicate a very good correlation between wear rate in 'single pass' abrasions and the ratio of  $\sigma/R_{Av}$  where  $\sigma$  is the standard deviation of heights and

$R_{Av}$  the average radius of curvature of the asperities (Fig 7). Tabor<sup>50</sup> has shown that  $\tan \theta \approx (\sigma/2R_{Av})^{1/2}$ .

The basic relationship (Eq (4)) suggests that abrasive wear will occur for all values of  $\theta$ . This is not the case and the notion of a critical angle for cutting has been suggested by Lancaster<sup>1</sup> and has also been incorporated into the theoretical treatments of the abrasive wear of ductile metals. Warren and Eiss<sup>22</sup> have carried out a detailed study of the critical angle for cutting in high load single pass abrasion debris deposited at the front of an asperity. The study involved the measurement of the angle of the debris surface formed with reference to the horizontal datum in the counterface over a large number of ridges. When no transfer of debris was detected this angle corresponded to the slope of the clean asperity,  $\theta$ . A tabulation of a large number of these angles, termed shear angles, reveals a characteristic minimum for a given polymer which is not a substantial function of load. Warren and Eiss argue that for each characteristic minimum shear angle there exists a somewhat larger critical slope for a given polymer. Typical values for minimum shear angles range from about  $2^\circ$  for pvc to an average of about  $8^\circ$  for nylon. The values of the critical slopes themselves are not known but the minimum shear angle is found to be proportional to the work to rupture. Since the average slope of typical rough surfaces does not generally exceed more than a few degrees, few asperities will be able to produce a chip in a single process. This is consistent with the rather small  $K$  values and suggests that debris formation may often be preceded by non-disruptive plastic grooving. Such a sequence has been proposed in particle erosion<sup>51</sup> and in the abrasion of metals<sup>52</sup>.

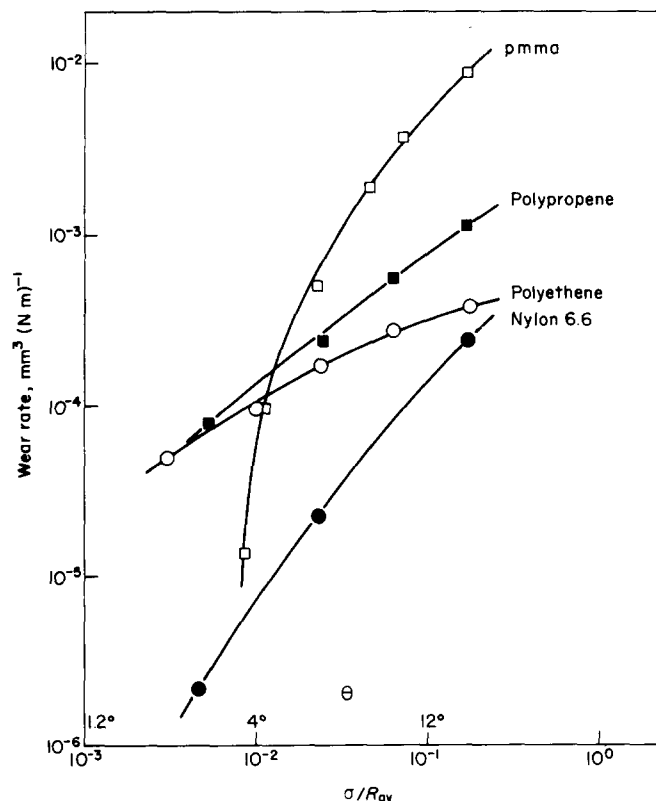


Fig 7 Single pass rates of wear against  $\sigma/R_{av}$  which is a measure of mean asperity slope<sup>1</sup>. The asperity slope  $\theta$  estimated from the relationship  $\tan \theta \approx (\sigma/2R_{av})^{1/2}$  is shown. The wear rate is a pronounced increasing function of the calculated mean slope

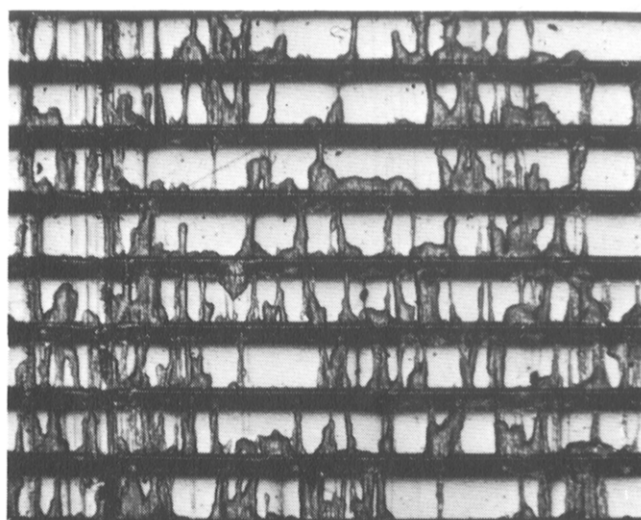


Fig 8 The characteristic highly drawn fibrils produced when ductile, potentially fibre drawing, polymers are slid over ruled metal surfaces such as diffraction gratings. The optical micrograph shows ridges which are ca  $5\mu\text{m}$  high at intervals of ca  $1\mu\text{m}$ . The polymer is ptfе and has been slid in a direction normal to the rulings from top to bottom ( $\times 100$ )

The experiments reviewed so far correspond to single pass abrasions where the debris is not allowed to accumulate in the surface roughness. Multiple traversals invariably lead to an effective reduction in roughness and wear particularly for ductile polymers. Ratner et al favour the use of gauze as an abrasive for this reason. The debris simply falls out of the back of the gauze. Highly ductile polymers such as ptfе also produce highly drawn fibrils ca  $0.2\mu\text{m}$  in diameter in the direction of sliding which span the peaks of asperities<sup>43</sup>. The fibrils may be several microns in length and are best demonstrated by sliding over diffraction gratings (Fig 8). The capacity of certain polymers such as ptfе to undergo substantial orientation has a consequence in adhesive or transfer wear (see later). Less ductile polymers such as pmma produce discrete simple shear-type chips at low energy indices ( $z/\mu W$ ). The mechanism of debris expulsion becomes of great importance in multiple traversals. It is known that such factors as the geometry of the contact, particularly its conformity, are important factors but a comprehensive treatment of these processes is clearly beyond simple analysis. The situation is further complicated where abrasive filler particles are incorporated within the matrix. There have also been suggestions in the literature that certain scales of roughness may actually reduce the rate of wear for certain transferring polymers.

To complete this section, reference is made to a number of recent studies of surface melting in semicrystalline polymers. Tanaka and Uchiyama<sup>53</sup> have made an interesting study of surface melting and its accompanying transfer of polymer to the counterface. For high density polyethylene (hdpe) molten layers of ca  $15\mu\text{m}$  are transferred to the counterface prior to gross melting of the polymer. Kar and Bahadur<sup>54</sup> and Arkles and Schireson<sup>55</sup> have published similar findings. When gross melting occurs Tanaka and Uchiyama<sup>56</sup> were able to account for the frictional work in terms of the viscous dissipation in the molten layer and suggested an extrusion of the melt as the major wear mechanism under these conditions.

## Interfacial wear

Interfacial wear results from energy dissipation within rather narrow regions adjacent to the interface. This topic includes the mechanisms of adhesive or transfer wear and chemical erosive wear. The frictional work is dissipated in a smaller volume and the rates and extent of the surface deformations are greater than those which exist in cohesive wear. This naturally creates a significant increase in local temperature in many cases. Unlike the previous classes of cohesive wear factors other than mechanical toughness, fatigue properties, geometric form and thermal properties are of significant importance. The frictional work originates from the adhesive forces which emanate from the contacting solids. In the cases of cohesive wear these forces produce the tractive stresses which are manifested in the formation of cracks at surface or subsurface flaws. In the present context these adhesive forces generate localised plastic surface deformation and the transfer of relatively undegraded polymers to the counterface in certain systems. In other cases these localised deformations and associated temperature rises produce chemical degradation of the polymer and often the transfer of degraded material. The two broad types of interfacial wear are sufficiently distinct to warrant separate discussion.

### Natural adhesive or transfer wear

The phenomenalism of adhesive wear has been described<sup>1-3,7-10,56-67</sup>. When certain polymers are slid over clean and smooth counterfaces the adhesion between the polymer and the counterface is of sufficient magnitude to inhibit sliding at the original interface. Instead the junctions rupture within the polymer itself and a layer of polymer is deposited upon the counterface in the form of a more or less coherent transferred layer. Subsequent traversals of the polymer over this film remove the transferred layer which is ultimately displaced from the contact. A further layer is deposited, the process repeats and the polymer surface is gradually worn away. The process is certainly more complex than described and contains numerous subtle features which belie simple description. The basic elements of this process will be identified and discussed separately:

- (a) the nature and magnitude of the initial adhesion between the polymer and the substrate;
- (b) the locus of the junction failure;
- (c) the thickness and molecular organisation of the transfer layer and subsequent changes during repeated deformations;
- (d) the final or equilibrium adhesive bonding of this film to the counterface after multiple deformations;
- (e) the mechanism of film removal; and
- (f) the displacement of transfer debris from the contact region.

These processes can be discussed only in the most general terms, although this does provide some understanding of the one particularly important aspect of transfer wear: the role played by filler particles.

#### (a) Initial adhesion

The initial junction strength will be a function of the interaction of the surface forces and the mechanical properties of the contact. For polymers the surface forces will be a combination of Van der Waals, coulombic and possibly hydrogen bonding forces. The precise role of coulombic

forces is in doubt<sup>3</sup>. The higher the surface free energy of the polymer the greater will be the adhesive forces although this is counterbalanced by the tendency of the high cohesive density solids to fail in a brittle manner with the result that the adhesive work is reduced. Polymers above their glass transition temperature will adhere more strongly for this reason. The ability of these materials to conform to minor surface imperfections coupled with the relatively low level of stored elastic strain will also facilitate stronger adhesion. In addition the cleanliness of the contact region will be an important factor. Very clean metal surfaces may promote chemical bonding and perhaps gross chemical degradation whilst efficient lubrication will suppress the direct contact of polymer and counterface.

#### (b) Locus of junction failure

Neglecting extensive mechanical and chemical degradation, it appears that essentially brittle and highly elastic cross-linked polymers tend to fail at the original interface. This category includes polymers below their respective glass transition temperatures and crosslinked systems. The significance of a glass transition at a sliding interface was discussed previously. Uncrosslinked systems above their glass transition temperature appear to transfer polymer although there are exceptions such as polypropylene<sup>61-67</sup>. The position of the shear plane in these systems is judged from the observed thickness of the transferred layer and is between about 10 nm and a few microns, depending upon the polymer and the sliding conditions.

A number of authors have sought a better insight into the properties which define the locus of failure beyond these vague suggestions based upon brittle/ductile response<sup>2,3</sup>. Jain and Bahadur<sup>57</sup> and Sviridyonok<sup>58</sup> et al considered the role of surface free energy and recently this factor has been reviewed by the author<sup>68</sup>. Pooley and Tabor and others have made connections with the frictional characteristics of the polymer<sup>7,61-67</sup>. Nevertheless a comprehensive account of this important feature of adhesive transfer is awaited as are the factors which control the transferred layer thickness when such layers form. These aspects are discussed further in the next section.

#### (c) Transferred layer: its thickness and molecular organisation

Transferred layers appear to be of four general types, three of which are relevant in this section and are cases where 'whole' or largely unchanged polymer is transferred without extensive chemical degradation. There may be marked changes in morphology but relatively little chemical degradation or chain scission is observed. The third group of transfer involves the deposition of chemical degradation products (see later) and perhaps low molecular weight components which have migrated to the surface. The 'bloom' on rubber surfaces is an example of the latter<sup>69</sup>.

A polymer such as high density polyethylene exhibits the three types of 'whole' transfer behaviour<sup>5</sup>. At low sliding velocities (ca 5 mm s<sup>-1</sup> or less) at room temperature high density polyethylene forms two types of transferred film when it is slid against a smooth clean counterface in air. At the onset of sliding the frictional force is quite high and a relatively thick, ca 0.1 µm, and reasonably highly drawn transferred layer is deposited. Once sliding has progressed about one contact diameter the friction force



decreases by perhaps 20% and a much thinner, ca 10 nm, but patchy transferred layer is produced<sup>70</sup>. The film is highly drawn in the direction of sliding as revealed by electron diffraction<sup>61–67</sup>. The thick film transfer has been designated as 'lumpy' or 'normal' transfer behaviour<sup>61–67</sup>. The thin film transfer which develops once sliding motion has developed is apparently restricted to what have been termed 'special' or 'smooth molecular profile' polymers. High density polyethylene, ultra high molecular-weight polyethylene and ptfе and possibly polyoxymethylene are the only known examples. In these cases the thin film transfer is restricted to a limited range of contact conditions. The introduction of surface roughness<sup>61–67</sup>, rotation coupled with sliding<sup>71</sup> (Fig 9) and radiation cross-linking<sup>61,67</sup> suppresses the thin film transfer and 'normal' transfer prevails. It is also believed that there is a critical upper velocity for a given temperature where the transferred film loses its highly drawn character<sup>16,54,72</sup>. Polymers other than the four cited above form a thick and rather unoriented transfer film during sliding and low density polyethylene is a typical example<sup>3,73</sup>. Apart from these two forms of transfer which are tentatively assumed to form under isothermal conditions there are also the transferred layers which form as a result of adiabatic frictional heating. The work of Tanaka has already been described in this context.

The factors which control the extent and nature of these layers are not yet established. The process has something in common with fibre drawing and in some cases involves substantial orientation of the polymer. In the obvious adiabatic case the mechanical and thermal properties of the polymer will define the shear plane and film thickness. At lower speeds adiabatic shear zones may develop within the polymer surface and hence produce a characteristic thickness. For the cases of thin film transfer where the layers approach molecular or morphological dimensions, it has been suggested that these factors are a controlling influence.

Once a coherent transferred layer has been deposited by multiple traversals over the counterface there is limited experimental evidence to suggest that further transfer of polymer upon the transferred polymer layer does not occur to any substantial extent. Sliding now occurs at the interface between oriented polymer layers. Wear is achieved if the original layer is displaced from the counterface so that free counterface is available for further transfer. We may however envisage the possibility of back transfer of polymer film on to the polymer specimen and effectively zero wear. The notion of a strong adhesive junction between the transferred layer and the counterface suppressing the overall wear process has been explored in the context of filled polymer composites<sup>74,75</sup> and is discussed in the next section.

#### (d) Transferred film/counterface interactions

In the absence of chemical degradation the adhesive forces will be of the type described in (a) and for pure polymers the strength of the adhesive junctions appears to be relatively low. The films may often be stripped off with pressure sensitive tape and by immersion in aqueous surfactant solutions. This relatively poor adhesion has been suggested as an important rate controlling factor in the overall rate of adhesive wear particularly in cases where spasmodic fluid lubrication occurs. This belief

emerges from studies on the influence of filler particles on the rate of wear of certain polymeric composites. A good composite material may provide a rate of wear of perhaps three orders of magnitude less than that of the virgin polymer and at the same time maintain approximately the same level of frictional work<sup>74</sup>. Recent studies indicate that effective fillers substantially increase the adhesion of the transferred layer to the counterface and hence reduce the rate of wear<sup>76</sup>. Before reviewing the evidence for this argument a number of general comments on filled composites are appropriate.

A wide range of filled systems have been studied and the important fillers are of the following types: carbons or graphites, inorganic glasses, transition metals and their chalcogenides and a number of high temperature polymers such as polyphenylene sulphide and polyimides<sup>2,77</sup>. Particle size<sup>76</sup> and size distribution<sup>76</sup>, hardness, aspect ratio<sup>74,78,79</sup> and concentration<sup>74</sup> are known to be important. In certain systems there is evidence for synergistic chemical action between mixed filler packages<sup>75,80</sup>. The filler package is generally tailored on the basis of empirical testing and its efficiency is sensitive to the type of polymer, the counterface and the environment. In many cases the filler particles will improve the thermal conductivity and creep resistance of the matrix. There is also an indication that certain high aspect ratio filler particles will tend to suppress the natural reorientation of the ptfе type of polymers during sliding<sup>81</sup>. Examination of sliding contacts provides a number of interesting general results. The surface of the matrix often appears to have an

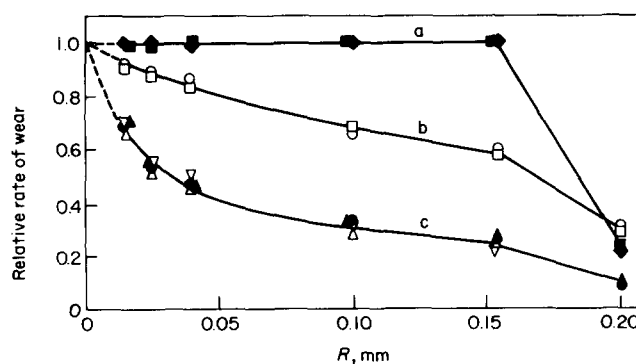
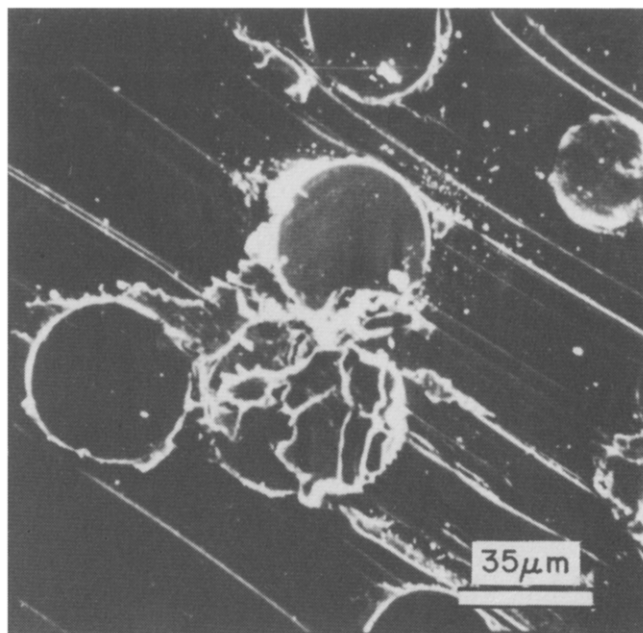


Fig 9 The peculiar effect of apparent rotation during linear sliding observed in the pin-on-disc sliding configuration. The relative rate of wear is the rate of wear for a particular wear track radius  $R$  divided by an estimate of the rate of wear at an infinite value of  $R$  for pure linear sliding. The latter is obtained by extrapolating the measured rate of wear as a function of  $1/R$  to  $1/R=0$ ; linear motion. The data are of two kinds. The relative wear rate is independent of the path radius for low density polyethylene and pmma (curve a). For ptfе and certain ptfе composites (curve c) and high density polyethylene and ultra high molecular weight polyethylene the relative wear rate decreases as the path radius decreases. The effect is apparently due to the rather complex sliding motion generated in the pin-on-disc configuration which disturbs the natural reorientation processes which occur at the sliding interface for ptfе and the linear polyethenes<sup>60</sup>. The sliding motion has the character of linear motion coupled with rotation about the load axis. The apparent rotation increases as  $1/R$  for a constant value of linear velocity. Sliding velocity  $0.5 \text{ ms}^{-1}$ , apparent constant pressure  $\sim 10^5 \text{ Pa}$



excess concentration of filler<sup>82,83</sup> and the filler itself suffers appreciable wear or deformation and stands proud of the surface and thus supports a significant fraction of the load<sup>2</sup>. The counterface is coated with a transferred layer of a type similar to that formed by the whole polymer. In addition the counterface topography is modified by the abrasive action<sup>1,84,86</sup> of the filler particles and there is often some evidence of chemical degradation of the sliding members (see later). The most efficient matrices in terms of wear resistance often produce the more strongly attached transferred layers and at the same time the most pronounced changes in surface topography. These judgements are necessarily subjective in view of the intrinsic difficulty in assessing the strength of adhesion and monitoring topography changes in the presence of transferred layers. It also appears that the high temperature polymeric fillers can achieve a reasonable suppression of the wear rate without the accompanying change in surface topography. Arkles<sup>82</sup> and Tanaka<sup>83</sup> have interpreted these trends in a simple fashion. As the matrix wears polymer is lost more readily than filler and eventually an array of protruding filler particles support a large fraction of the load and slide over a surface which is lubricated with a thin film of polymer (Fig 10). The rate of wear is then a strong function of the wear characteristics of the filler. The present author and his colleagues have suggested that in addition to this aspect the filler particles also promote the formation of a more strongly attached transferred layer to the counterface<sup>5</sup>. Transfer layers formed by filled composites do adhere more strongly to the counterface and such a layer will also maintain a low rate of wear when an unfilled polymer is slid over its surface<sup>75</sup>. There is also limited evidence for the beneficial effects of minor chemical reactions promoted in the contact region by certain transition metal oxide fillers. It has been suggested that these fillers induce mild degradation of the polymer and create strong valence bonds between the transferred layer and the counterface. This notion is developed further in the next section<sup>5,80</sup>.

An alternative suggestion is that the change in roughness of the counterface created by the fillers enhances the adhesion of the film. With carbon filled composites it is observed that only those carbons which actually abrade the counterface produce viable composites<sup>74</sup>. Lancaster has reviewed the role of abrasion in the formulation of composites<sup>1,86</sup>. Three factors emerge from his and our own work. First, the abrasion will clean the counterface and ensure close contact between clean metal or oxide and the polymer film<sup>74</sup>. The same process will, of course, abrade the transferred layer. The abrasion process may also produce an optimum surface roughness which facilitates good adhesion. For pure polymers the wear rate often seems to show a minimum at a critical value of counterface roughness<sup>84,87</sup>. The reason for this effect is not clear but may be associated with a stress intensification at the asperities which locally soften and mechanically deform the polymer to provide a stronger junction. The same effect is also thought to explain, in part, the action of the filler particles. Again the stress intensification is likely to improve the connection between the polymer and the counterface even in the absence of chemical degradation. In these cases, although it is the level of local stress which is important, it also appears that for one system, carbon filled-ptfe, there is a connec-



*Fig 10 Scanning electron micrograph of the worn surface of a ptfe specimen filled with 10% by volume of ca 20  $\mu\text{m}$  glass spheres. The specimen had been sliding for several hours against a steel counterface and the wear of the glass spheres is very evident. What appears to be 'back transfer' of polymer film is observed on many particles. Also notable is the fact that the particles appear to stand proud of the ptfe matrix. It is not known whether this relief is so pronounced or indeed exists within the contact or is due to stress relaxation during unloading and sample preparation. Sliding direction: north west. Specimen coated with silver prior to examination to reduce electrical charging*

tion between the total frictional stress and the rate of wear<sup>84</sup>. As the counterface roughness is progressively increased the rate of wear decreases and the frictional stress increases. The former achieves its minimum and the latter a maximum at approximately  $0.4 \mu\text{m } R_a$ . Apparently the greater the frictional work dissipated in the contact the lower is the rate of wear (Fig 11). Recently Eiss and Bayraktaroglu<sup>88</sup> have noted the transition from transfer wear to abrasive wear for low density polyethylene.

#### *(e) Mechanism of film removal*

Electron microscopic studies of transferred films of materials like ptfe indicate substantial orientation<sup>61-67,89</sup> and that surface tractions can rumple the layer and remove roughly elliptical patches of film<sup>5,75</sup>. The underlying mechanisms have not been investigated but because of the layered and oriented nature of the film transverse cracking and delamination<sup>90</sup> are likely elements (Fig 12). The observed back transfer of platelets of film are consistent with this mechanism although the debris will certainly be heavily worked in the contact after displacement from the surfaces. In filled systems of transferring polymers evidence of microabrasion is evident and the debris is often observed to be in the form of rolls or scrolls (Fig 13)<sup>5</sup> reminiscent of the phenomena described by Aharoni<sup>29</sup> and Reznikovskii and Brodskii<sup>28</sup>.

Apart from these physical processes it is also likely that the film will lose coherence through chemical degradation and chain rupture. Mass may then be lost through the vapour phase.

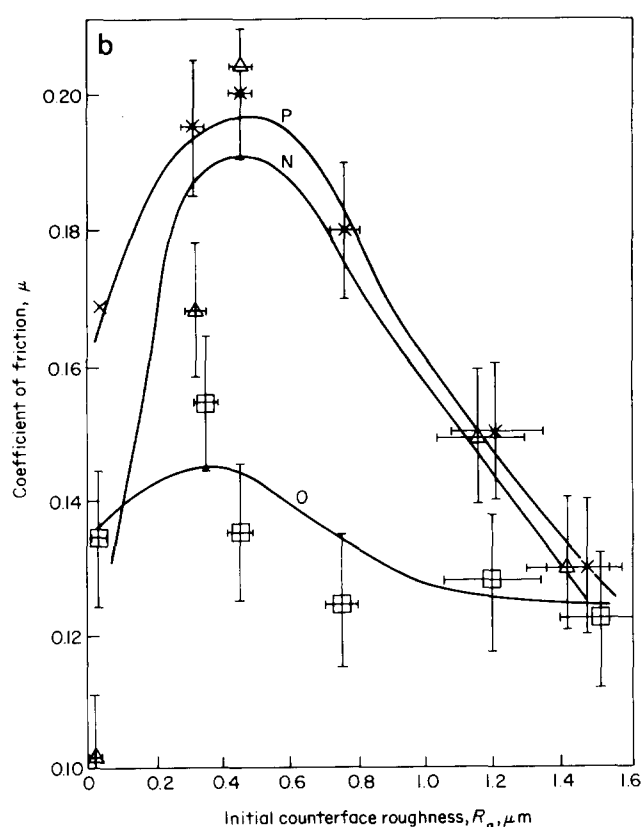
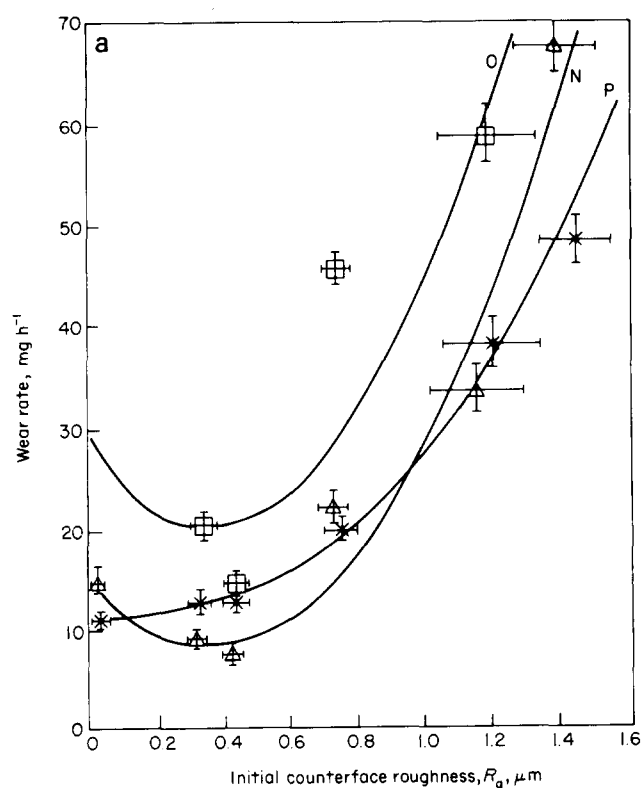


Fig 11(a) Wear rate and (b) friction coefficient for three carbon-filled ptfe specimens as a function of the initial roughness of the steel counterface. The only measurement of roughness is the  $R_a$  value. The roughness was introduced by shot blasting. Little change in surface topography was noted during the time of the wear experiment: ca 8h. Within the limited experimental evidence, the friction is a maximum and the wear rate a minimum at an  $R_a$  value of ca 0.4  $\mu\text{m}$ . The three graphites have rather different particle

size and aspect ratio and are present at 10% by weight. Sliding speed ca  $2\text{ms}^{-1}$ ; nominal contact pressure ca  $10^5$  Pa; pin-on-disc sliding configuration. N: nuclear grade; P: polar; O: oleophilic. Polar and oleophilic grades are derived from nuclear graphite by milling in air and oil respectively. Oleophilic has the form of thin flakes whilst the parent graphite and the nuclear graphite are more regularly shaped



Fig 12 Appearance of a transfer film of high density polyethylene produced on a steel counterface from a metal oxide filled high density polyethylene composite. Sliding direction: right to left. The classical transverse cracks and buckled film are noticeable. It is not known how many layers of transferred film are deposited on this surface. Image produced by two stage carbon replication<sup>64</sup> and transmission electron microscopy

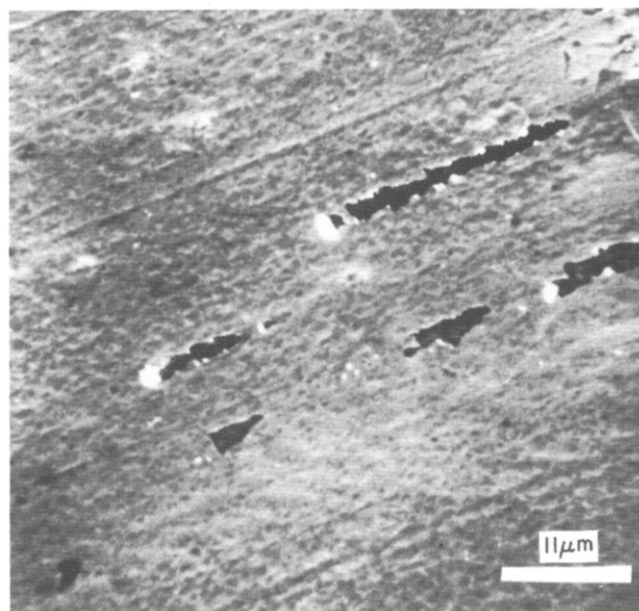


Fig 13 sem of the transfer film produced by a composite of ptfe and 10% by volume of ca. 20  $\mu\text{m}$  diameter glass spheres. The transferred film has been abraded and 'rolls' of film are evident at the ends of the microwear tracks. The film was formed by rubbing the composite against a relatively smooth steel counterface sliding at  $2\text{ms}^{-1}$ . Nominal contact pressure and temperature ca  $10^5$  Pa and ca  $25^\circ\text{C}$  respectively. Specimen coated with silver

*(f) Debris displacement*

In many circumstances a highly conforming contact, such as in a thrust bearing, does not allow the wear debris to escape from the contact. For pure ptfe the wear debris acts as a 'lubricant' and the wear rate is reduced under certain circumstances. This is the so-called 'third body'. A recent paper<sup>91</sup> indicates that the converse may occur with a bronze filled ptfe when it is slid as a metal backed film against a mild steel in a thrust-washer configuration. The inclusion of radial debris grooves produces a significant reduction in wear rate at high loads. Allowing the debris to escape leads to a reduction in the rate of wear. The effect is not observed with a glass fibre filled ptfe.

These experiments serve to highlight the technical importance of debris expulsion. The mechanisms are clearly complex and a better understanding of the processes involved would be of value in the design of bearings as well as in the correlation of wear data obtained from different sliding configurations. This process is particularly important in fretting and reciprocating wear.

**Chemical wear**

An element of chemical degradation is most certainly present in all wear processes. It ranges from mild chain scission in, for example, the gentle fatigue abrasion of elastomers to the gross decomposition developed in filled-crosslinked resins under intense loadings. Richardson<sup>14</sup> has briefly reviewed part of this diverse topic. The chemical facets of wear have been particularly popular with Soviet workers<sup>9,10,92</sup>. Even in the most favourable circumstances there is doubt as to the precise role played by the chemical reactions in the overall wear process. Invariably bulk thermal decomposition or oxidation data are applied to reacting contacts without a detailed knowledge of the transient thermal conditions, the pressure, the reactants and their availability. Additional complications arise from the uncertain effects of strain activation, the catalytic effect of clean metal surfaces and the part played by potentially active fillers. A number of studies do however shed some light on the relative importance of these factors.

Rhee and Liu<sup>93</sup> have applied a combination of surface temperature calculations and 'static' thermal degradation data to rationalise the wear behaviour of a range of brake materials. A number of workers, including Buckley and Johnson<sup>94,95</sup>, Pocock and Cadman<sup>96</sup>, have used surface analytical tools such as Auger and esca spectral analysis to monitor the chemistry of the wear debris and transferred layers. A number of studies have also been carried out in vacuum and the chemistry of the gaseous decomposition products have been examined<sup>58,97</sup>. Other studies have attempted to relate changes in environment and the associated change in wear rate to chemical reactions<sup>76</sup>. In this context the influence of certain fillers on the wear behaviour of high density polyethylene and ptfe is of interest. The synergistic action of lead and copper oxide fillers has been mentioned previously<sup>75,80</sup>. Static decomposition and oxidation experiments using differential-scanning calorimetry and thermal gravimetric analysis indicate that the most efficient filler combinations also produce a very mild gas phase oxidation at around 150°C<sup>98</sup>. It has been suggested<sup>5</sup> that this mild reaction may facilitate the formation of effective bonding between

the transferred layer and the counterface and hence reduce the level of wear. Excessive chemical attack produces pronounced wear as is indicated in the work carried out with very clean counterfaces in vacuum<sup>99</sup>. The high rates of wear reported in 'bone' dry, closed environments for ptfe composites may be a result of the creation of very clean aggressive metal surfaces<sup>100</sup>.

**Conclusions**

The processes of wear are not well understood and the subdivision of polymer wear is no exception. In many cases the rate of wear may be correlated with certain bulk properties such as mechanical toughness or chemical reactivity if a particular mechanism is supposed to prevail. Even in the most favourable and extensively studied cases, for example, the abrasive wear of elastomers, a number of important features of the wear process elude explanation. We may be able to rationalise the rate of damage of the surface in terms of fatigue cracking but we cannot *a priori* specify the scale of the wear debris. In less well defined processes like transfer wear even the phenomenology is only sketchily understood. A broad knowledge of the mechanical and chemical properties of polymers, coupled with an appreciation of the likely conditions existing in the contact region, provides a framework which has limited predictive capacity. Even then we rely heavily upon the extensive empirical precedents developed in previous wear studies. This level of insight while in some senses depressingly unrevealing does however afford a sufficient basis for identifying those fundamental aspects deserving of further study.

**Acknowledgements**

I wish to thank Dr M.D. Steward for preparing a number of the electron micrographs included in the text. I am also indebted to Prof. D. Tabor, F.R.S. for valuable and stimulating comments during the preparation of this article.

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## Conference Reports

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8–10 April 1981, Leicester, UK

### 8th International Gas Bearing Symposium

Organised by Leicester Polytechnic in conjunction with BHRA Fluid Engineering, the 8th International Gas Bearing Symposium was held at the delightful Scraftoft Campus just out-

side Leicester. Although it only attracted modest numbers in attendance, this occasion marked 21 years since the first symposium and was full of interest with sessions on

Analytical Modelling of Gas Bearings, Experimental Studies, Design and Application.

The greatest impact came from the Japanese delegation who contributed no less than eight papers revealing a concerted effort on all aspects of gas bearing technology. The papers presented were equally impressive and ranged from gas bearing applications