# Grooves in scratch testing

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For a number of polymers with a variety of chemical structures and different properties, we have performed scratch-resistance tests and investigated the profiles of the grooves formed using a profilometer. Three main kinds of material response are seen: plowing; cutting; and densification. The cross-sectional areas of the grooves include the groove and side top-ridge areas. The latter are smaller than the former, an indication of densification at the bottom and the sides of the groove; the effect can be connected to molecular dynamics simulations of scratch testing. The sum of the groove and top-ridge areas is the highest for Teflon, thus providing another measure of its poor scratch resistance. The Vickers hardness of the polymers was also determined. An approximate relationship exists between the hardness and the groove area. An unequivocal relationship between the hardness and the total cross-sectional area of the material displaced by the indenter is found. The resulting curve can be represented by an exponential decay function.

## I. INTRODUCTION

The economic well-being of industry is dependent on material wear, as argued eloquently by Rabinowicz.[1] As noted in an earlier article of ours,[2] the problem is particularly serious for relatively soft polymer surfaces.

Wear has been defined as the loss of solid material from the rubbing surface due to mechanical interaction at asperities.[1] However, material displacement on the surface without any changes in weight or volume also occurs.[3] Such displaced material can either mitigate subsequent wear by material transfer, by blunting of the asperities, or else by becoming a part of the later more pronounced wear. It is generally recognized that the most common types of wear of polymers are those caused by abrasion, adhesion, or fatigue.[4]

There is ongoing work on mitigating wear by a variety of means; for a review of polymer tribology see Ref. 5. As an example, both γ-irradiation and the addition of carbon black as a filler have been used to achieve lower friction and higher sliding wear resistance.[6] Another line of work aims at an improved understanding of wear mechanisms. The surface-damage-maps approach developed by Briscoe and coworkers[7] belongs to this category. Important here is the fact, analyzed by Maeda et al.,[8] that for hard solid sliding over a soft material (polymer) the damage occurs concurrently with energy dissipation.

Our work belongs to the second category defined above: an understanding of mechanisms rather than an improvement of specific polymers. For a variety of polymers with different chemical structures, we investigated surfaces created by a diamond indenter in scratch-resistance testing.[2,9–14] One can perform single scratch tests[9] or else determine sliding wear by multiple scratching along the same groove. In either case, one obtains two values, the instantaneous or penetration depth $R_p$, and after a time the final or healing depth $R_h$. We have found in sliding wear tests that there is the phenomenon of strain hardening[11]: above a certain number of scratches [e.g., 10 (the number depends on the applied load)] in most polymers, further scratches do not affect the recovery depth $R_h$. A diagram of that depth as a function of the number of scratches reaches a horizontal asymptote.

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While in consecutive scratches in sliding wear tests the indenter interacts with increasing surface areas inside the groove, this fact alone cannot explain strain hardening. Smaller increases of the recovery depth in consecutive runs can be foreseen, but no increases at all are not expected. Therefore, the present article reports a first attempt to elucidate the mechanism of material displacement in single-scratch tests. We presume that an improved understanding of those mechanisms will later help us to explain the strain-hardening phenomenon in multiple scratching tests. While nanoindentation attracts much attention, much less understanding of scratch behavior has been achieved to date. Some of that understanding comes from molecular-dynamics computer simulations of scratch testing of polymer surfaces.[15] The simulations provide us with continuous curves of the depth of each surface segment on the indenter path as a function of time, $R(t)$. This is in contrast to experiments that give us only two average values for the entire material, $R_p$ and $R_h$. From the simulation results, one can get the bottom (lowest) values for each segment and average them, and, similarly, average the horizontal asymptotic values at the end of each curve; thus, one obtains the respective equivalents of experimental $R_p$ and $R_h$. At the end of Sec. IV, we shall connect some of the present experimental results to those from simulations.

Both $R_p$ and $R_h$ have been used to characterize scratch resistance.[2,6] One can also define[9] the percentage recovery:

$$f = (R_p - R_h)/R_p \times 100 \quad . \tag{1}$$

## II. EXPERIMENTAL

Materials selection was based on wide ranges of their mechanical properties and a variety of applications. Polystyrene (PS) was purchased from Aldrich Chemicals Co. (Milwaukee, WI). Polycarbonate (PC) and polytetrafluoroethylene (PTFE) were supplied by the Dow Chemical Co. (Freeport, TX) Polypropylene (PP) was supplied by Philips (Amsterdam, The Netherlands). Low-density polyethylene (LDPE) was supplied by Huntsman (Salt Lake City, UT). Polyethersulphone (PES) was supplied by Solvay Engineered Plastics (Mansfield, TX).

To prepare grooves on the polymer surfaces, we have used a Micro Scratch Tester from CSEM Instruments (Neuchâtel, Switzerland) in a single-scratch mode. The procedure and instrument used have been described in detail before.[2,6,9] A conical indenter with a diamond tip with a radius of 120 μm and conical angle of 90° was drawn over the polymer surface, the load applied was 15.0 N. The scratch speed was 5.0 mm/min. The scratch length was 5.0 mm.

A passage of the indenter results in the formation of groove and also in the formation of top ridges along both sides of the groove. Surface profiles across the groove made on each of the polymers were determined using a profilometer (Model Surtronic 3 +; Rank Tailor Hobson Ltd., Leicester, UK). Each such profile was determined perpendicularly to the side of the groove and through the center of the groove. The depth $D$ and the area of the groove were thus determined. We distinguish here between the area below the original planar surface of groove $A_i$ (inside) and the area of the ridges $A_o$ (outside). The subscripts stand for inside and outside, respectively.

Vickers hardness testing was performed in air at room temperature (24 °C) using a hardness tester (Model HMV-MIII; Shimadzu Corp., Kyoto, Japan). The shape of the indenter is pyramidal. The indentation load was 5.0 N, and the dwell time at the maximum load was 5 s for each indentation.

## III. PROFILES OF SCRATCH GROOVES

Figures 1–4 show cross-sectional profiles of a scratch groove on PES, LDPE, PTFE, and PS surfaces, respectively. We see in the profiles the pileups or top ridges along the sides of the groove, apart from the groove plowed by the indenter. The formation of the ridges implies the deformation mode of wear according to the traditional classification.

We also see, in Fig. 3 in particular, that the surfaces that were not touched by the indenter are not smooth on that scale. We have measured the groove area $A_i$ and the top-ridge area $A_o$ using the flat surface outside of the scratch trace as the baseline. The sum of these two areas provides us with the total area displaced by the indenter $A_{tot}$, that is

$$A_{tot} = A_i + A_o \quad . \tag{2}$$

We include only selected profiles for brevity (Figs. 1–4), but similar profiles are observed in other polymers. LDPE is the exception in this case. Only very tiny ridges are formed, as seen in Fig. 2. Numerical results are summarized in Table I.

A comparison between groove areas and top-ridge areas among the polymers we have investigated shows that the groove areas are much larger than the top-ridge areas in the cases of PC, PES, LDPE, and PTFE. In the case of

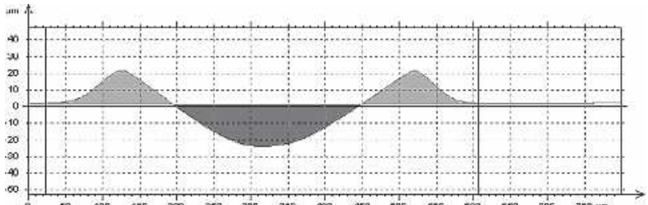

FIG. 1. A profile of a scratch trace on a PES surface for the applied load of 15.0 N. The profile is perpendicular to the side and goes through the center of the groove.

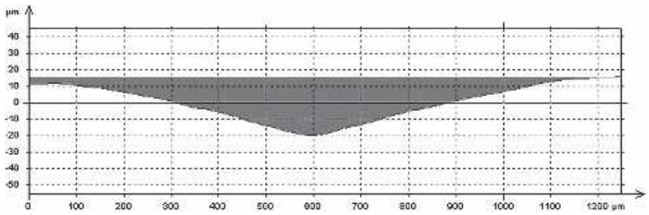

FIG. 2. A profile of a scratch trace on a LDPE surface. Other details are as in Fig. 1.

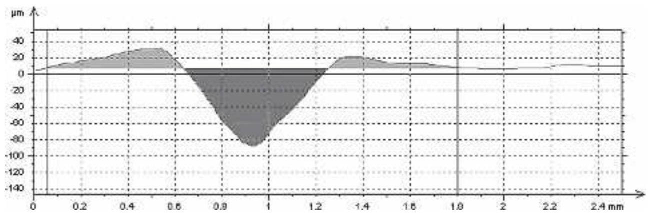

FIG. 3. A profile of a scratch trace on a PTFE surface. Other details are as in Fig. 1.

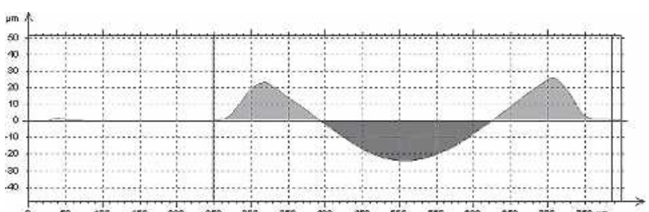

FIG. 4. A profile of a scratch trace on a PS surface. Other details are as in Fig. 1.

TABLE I. Results for a T5.0 N diamond indenter.

| | $D$ (μm) | $A_i$ ($\mu m^2$) | $A_o$ ($\mu m^2$) | $A_{tot}$ ($\mu m^2$) | $h_{Vickers}$ |
|---|---|---|---|---|---|
| PC | 30.5 | 5953 | 1071 | 7024 | 159 |
| PP | 29.8 | 6778 | 5460 | 12238 | 109 |
| PS | 24.4 | 3584 | 3425 | 7009 | 205 |
| PTFE | 95.0 | 32632 | 10595 | 43227 | 76 |
| PES | 25.6 | 4189 | 2850 | 7039 | 185 |
| LDPE | 35.6 | 19861 | 13 | 19874 | 93 |

PS, the groove area shown is comparable to the top-ridge area; the difference between these values is for PS < 5%. This might be related to the fact that PS is much more brittle than the other polymers[16]; we shall discuss this issue in more detail below after presenting more results.

As discussed by Rabinowicz,[1] largely on the basis of the results for metals, the material removal from the surface via deformation during hard surface sliding on a soft surface, called "abrasive wear," can occur by several deformation modes including plowing, wedge formation, and cutting. Myshkin et al.,[4] in Homel, Belarus, have concluded that the polymeric materials exhibit two prominent modes of deformation. The first is the plowing mode, in which a material is displaced sideways to form a top ridge but no material is removed. The second is cutting, in which the material displaced is removed as very small pieces, the main mechanism of wear. Our results, which are shown in the figures, indicate that both phenomena take place. The cutting process seems to occur together with the plowing process. The top ridges can contain both material pushed to the side and some material removed from the groove by cutting. However, densification is the third process we need to consider.

## IV. DENSIFICATION AND HARDNESS

Our assumption that densification occurs during the sliding of the diamond indenter deserves elucidation. Yoshida and co-workers[17] have discussed the densification of glasses caused by indentation. Now consider the findings of Bhushan et al.[18] that microhardness measurements of worn metal samples show a 10%–80% increase of hardness in the worn layer. While the behavior of the metals is different from that of polymers because the latter are viscoelastic, a possible connection between the characteristics of the groove profiles we have obtained with hardness determination seemed worth pursuing.

The Vickers hardness ($h_{Vickers}$) results are listed in the last column of Table I. Inspection of the results in Table I shows that polymers with higher hardness exhibit lower depths and smaller indentation areas than the ones with low hardness. Therefore, we have plotted the groove area $A_i$ displaced by the indenter as a function of $h_{Vickers}$ in Fig. 5. The plots can be approximately represented by an exponential decay function. Because the groove area $A_i$ decreases with hardness, this fact seems to provide indirect support to our hypothesis of densification inside the groove.

Given the results presented in Fig. 5, we have also plotted the outside cross-sectional area $A_o$ as a function of $h_{Vickers}$, and then repeated the operation with the total area $A_{tot}$. Both curves are shown in Fig. 6. The plots of

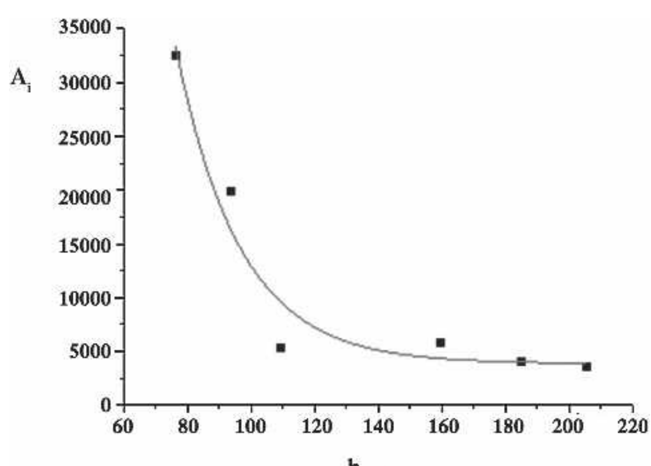


FIG. 5. Groove area $A_i$ as a function of $h_{Vickers}$.

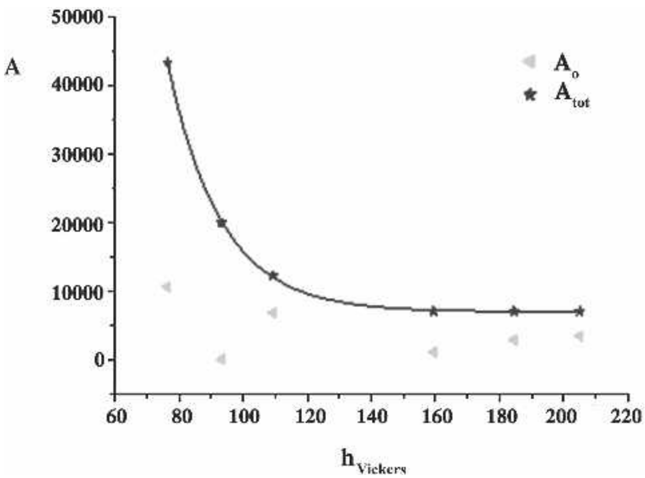


FIG. 6. $A_o$ and $A_{tot}$ as a function of $h_{Vickers}$.

$A_o(h_{Vickers})$ does not show a clear regularity. At the same time, the $A_{tot}(h_{Vickers})$ diagram represents a continuous descending curve, which seems to reach a plateau for high hardness values. All experimental points lie "exactly" on the curve: there is no scatter. The highest $A_{tot}$ value by far is that for PTFE, providing one more quantitative measure of the poor scratch resistance of Teflon (DuPont, Wilmington, DE). The $A_{tot}(h_{Vickers})$ curve can be represented by the equation

$$A_{tot} = 6960 + 3.56 \exp(-0.06\ h_{Vickers}) \quad . \qquad (3)$$

Equation (3) and the results in Fig. 6 behoove us to explain why there is such a clear relationship between $A_{tot}$ and $h_{Vickers}$ but not between $A_o$ and $h_{Vickers}$. Return now to Table I. In most cases, we have $A_i > A_o$. That is, the material removed by the indenter from the indenter path did not all go to the top ridges on the sides. Scanning electron microscopy of our samples tells us that little debris is formed, so that the cutting resulting in wear is insignificant. Thus, densification at the bottom and the sides of the groove is at least a plausible explanation. Moreover, the molecular-dynamics computer simulation results tell us that higher chain connectedness and higher entanglement density increase the resistance to scratching.[15,19] Because the densification increases both connectedness per unit volume and the entanglement density, we have the simulation results supporting the densification hypothesis.

A notable exception where $A_o \approx A_i$ is PS. That is, in PS practically all of the material moved by the indenter ends in the top ridges on both sides of the groove; there is no densification. We recall the definition of brittleness[16] according to which PS is much more brittle than most polymers.

## V. CONCLUDING REMARKS

Cross-sectional groove profiles obtained from single-scratch testing were investigated. Apart from the grooves, top ridges along the sides of the groove were also evaluated in terms of cross-sectional surface areas. According to classic tribology, the main mechanism of wear due to the sliding of an indenter on the polymer surface is the deformation mode of wear. However, the top-ridge areas determined from the profiles are not equal to the groove areas, with PS as a notable exception. We explain the behavior of materials other than PS by densification resulting from the sliding of the indenter. Moreover, we have demonstrated a connection between the total area displaced by the indenter and the hardness of polymeric samples, a relationship that is valid for all materials including PS, despite a large variety of properties. We infer that the total cross-sectional area is a useful tribological parameter, beyond the usually used wear volume or the weight that is worn away.

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