Scratch and Indentation Tests on Polyoxymethylene (POM)

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ABSTRACT: Scratch and indentation tests were performed on a polyoxymethylene homopolymer that was molded using three different mold temperatures. The different microstructures that developed during processing were studied by examining two samples for each mold temperature at different depths. During the scratch tests, the normal and the tangential force were recorded. The tests on the "as-molded" surface, in comparison to those that were polished until 1 mm of the material was removed, showed extrema of the normal force at a scratch depth that correspond to the interface of different regimes in the microstructure. The first extremum was considered to be caused by the breaking of the skin layer of the polymer (as a result of the rapid cooling process in the mold). Further extrema correspond to the permeation of the transition zone of the indenter into the spherulitic core of the sample. Indentation tests that were made on the same samples showed that the skin had a slightly lower hardness than the bulk of the polymer and that the difference in hardness decreases with increasing mold temperature. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1985–1996, 1997

Key words: polyoxymethylene; wear rate; microindentation; sclerometer; scratch test

INTRODUCTION

Polyoxymethylene homopolymer (POM; DELRIN® of DuPont), a thermoplastic material, is used in many applications in which friction and wear are critical issues. The study presented here was part of a project in which the abrasive wear resistance of POM as a function of the material's microstructure was of particular interest. In order to get a basic idea about the active abrasive wear mechanisms, single scratch tests were carried out by the use of a scratch testing device (sclerometer). In particular, scratching was realized on six different types of samples: DELRIN® 100* processed at three different mold temperatures (20, 80, and 120°C) and by two kinds of surface preparation.

The advantage of scratch hardness over indentation tests is the possibility of studying hardness variations along the scratch. The hardness of different phases can be determined by making one single scratch.[1] Hence, hardness differences between different morphological regions of POM (as a result of different thermal histories) should be detectable.

Furthermore, if the hardness value is used to predict abrasion resistance, then scratch tests, because they are akin to the abrasion process in

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* DELRIN® 100 is the trade name of Du Pont de Nemours for neat POM with high molecular weight.

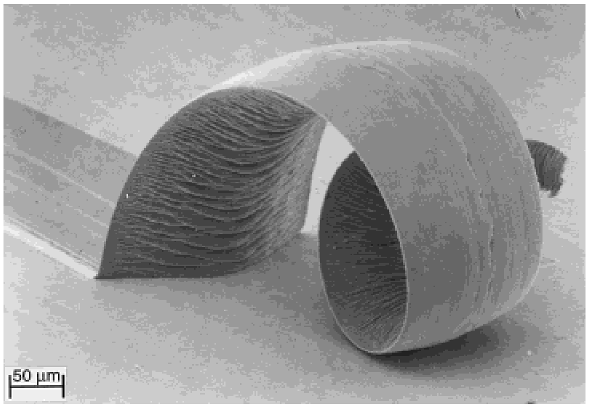


Figure 1 Curl of a scratch on DELRIN® 500 that was made under an angle of 3.4°, parallel to the mold filling direction.

many respects, should correlate better than ordinary indentation measurements.[2] Figure 1 shows an example of a POM curl that has built up during such a scratching experiment.

Additional indentation tests were also made using a normal Vickers indenter mounted on the scratch testing device (sclerometer).

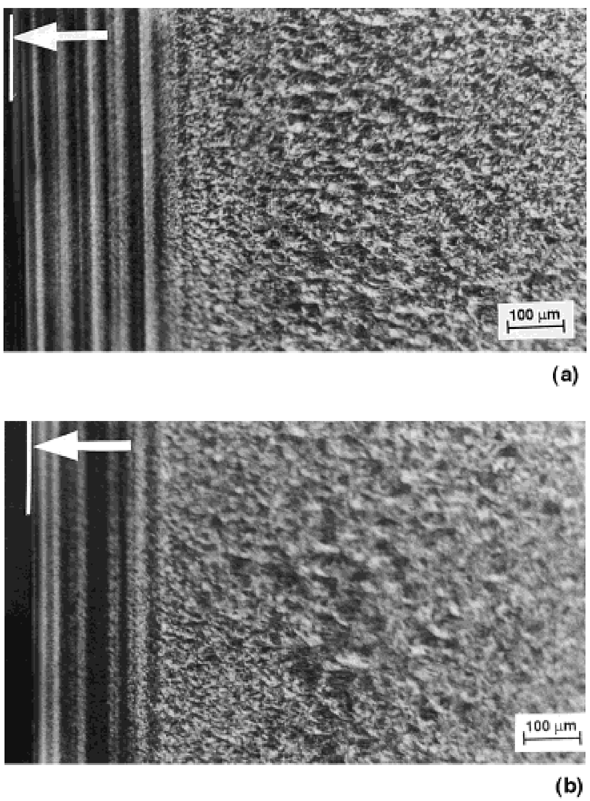


Figure 2 Optical micrographs of a POM bars processed at (a) 20°C, (b) 80°C, and (c) 120°C mold temperatures. The arrow indicates the surface of each sample.

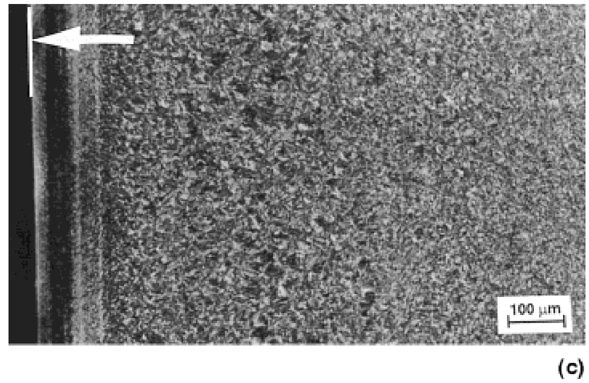


Figure 2 (*Continued*)

SAMPLES

Figure 2(a–c) show the different zones in the microtome cross sections of three injection molded POM bars. They demonstrate quite clearly how

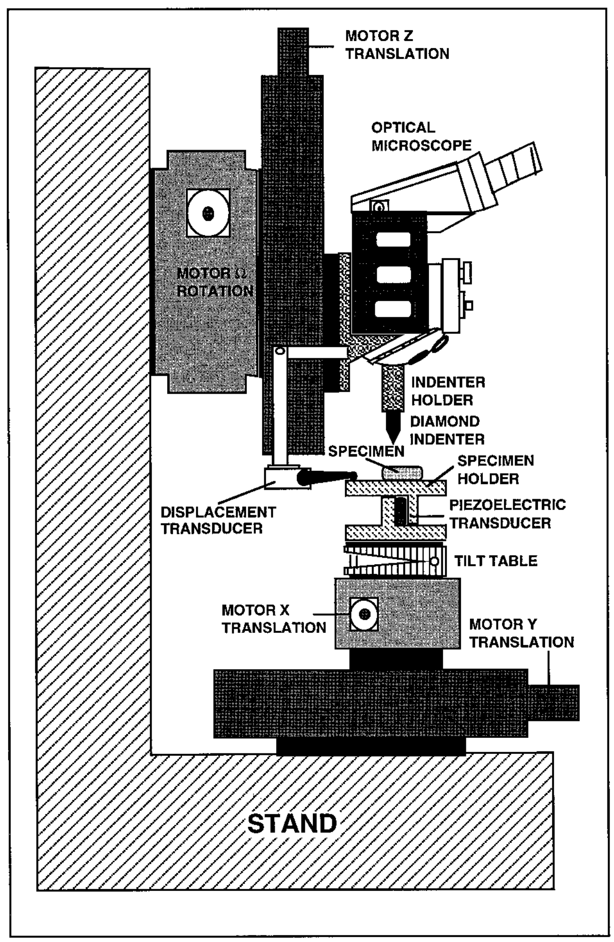


Figure 3 Experimental setup.

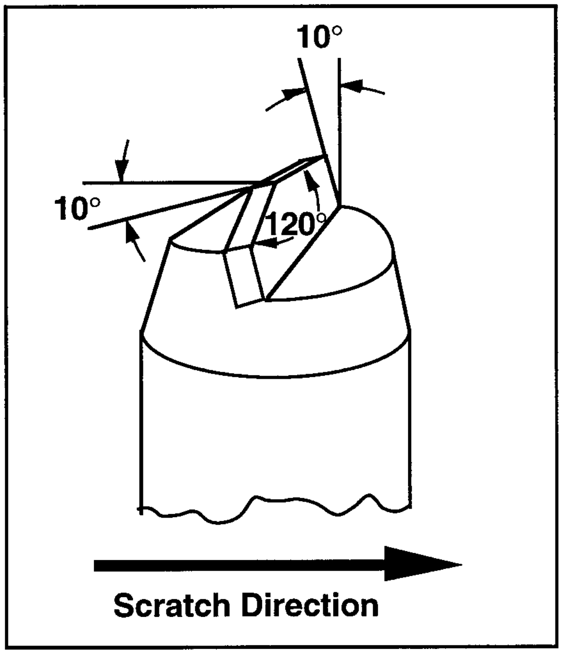


Figure 4 Shape of the scratch indenter used for all scratch tests. The opening angle of the indenter of 120° provides a final scratch depth of approximately 15–25 μm presuming a tilt table adjustment of 0.6°. It is obvious that the efficiency of scratch wear is not directly comparable to abrasive wear since the sharp edges of the diamond indenter are not implicitly comparable to asperities of, for example, a steel counterface.

the morphology of POM is affected by the mold temperature. Three separate regions can be identified: skin, transition zone, and spherulitic zone. The thickness of the skin and the transition zone, as well as the size of the spherulites, depend on molding conditions, such as melt and mold temperature, mold pressure, and screw forward time (SFT). The latter refers to the time over which the mold pressure is maintained during the injection molding process.

The cross sections shown in Figure 2 are from cuts of the different bars, taken at the opposite side of the injection gate. The background is dark brown due to the fact that polarized light is used. The arrow indicates the surface of each sample. It is seen that the sample molded at 20°C [Fig. 2(a)] has a thick (ca. 25 μm) transparent blue surface layer. In the case of the 80°C [Fig. 2(b)] sample, this region is only 9.1 μm thick, and the sample that was molded at 120°C [Fig. 2(c)] has no transparent zone. The following three distinct zones can be distinguished: the transparent zone, which will be referred to as the skin; a transition zone; and the spherulitic zone of the part, which will be referred to as the bulk.

To compare the scratch behavior of the as-molded surface and on the bulk polymer, two samples (bulk and skin) were cut out of the bars in the same region where the microtome cuttings were taken. The bulk samples were machined until 1 mm of material was removed. In order to obtain a comparable surface roughness, both types of samples were mounted in diallyl phthalate (short-glass-fiber-filled) and polished with 1-μm diamond paste and ethanol. The skin samples were only slightly polished to remove less than 1 μm of material.

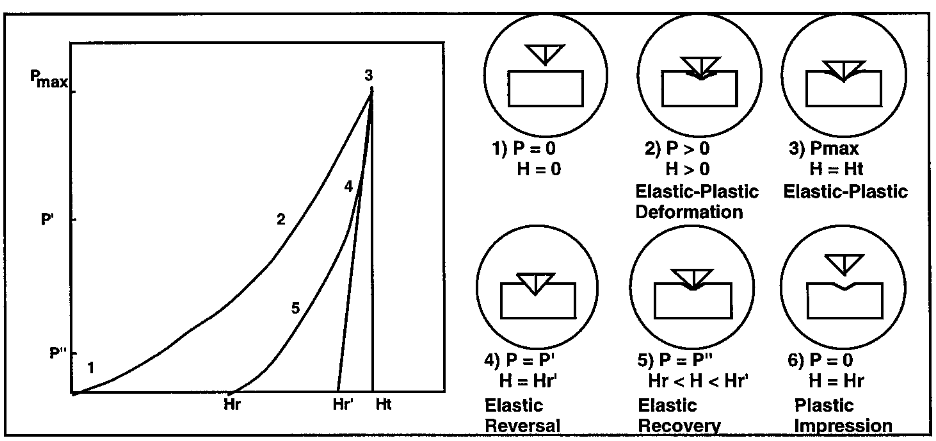
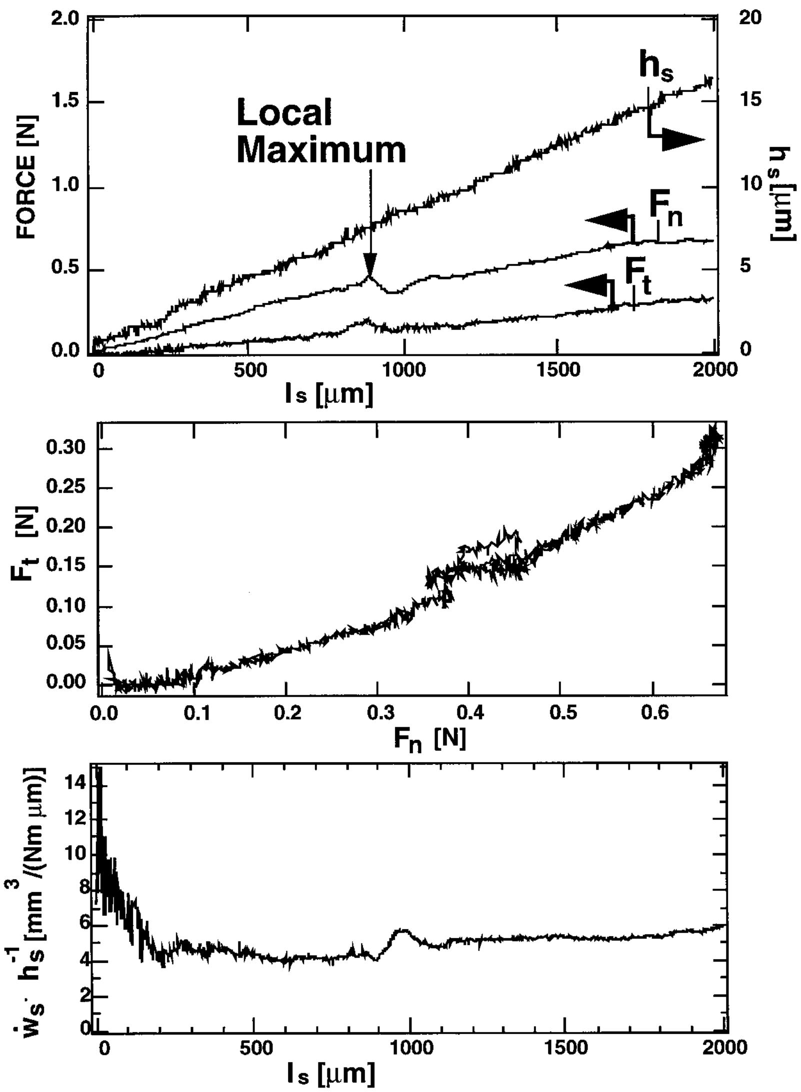


Figure 5 Typical slope of pressure versus depth during an indentation test demonstrating the difference of the measured values H_r, H_t and H_r' (see Table I).

Table I Results of Indentation Tests and Constant c

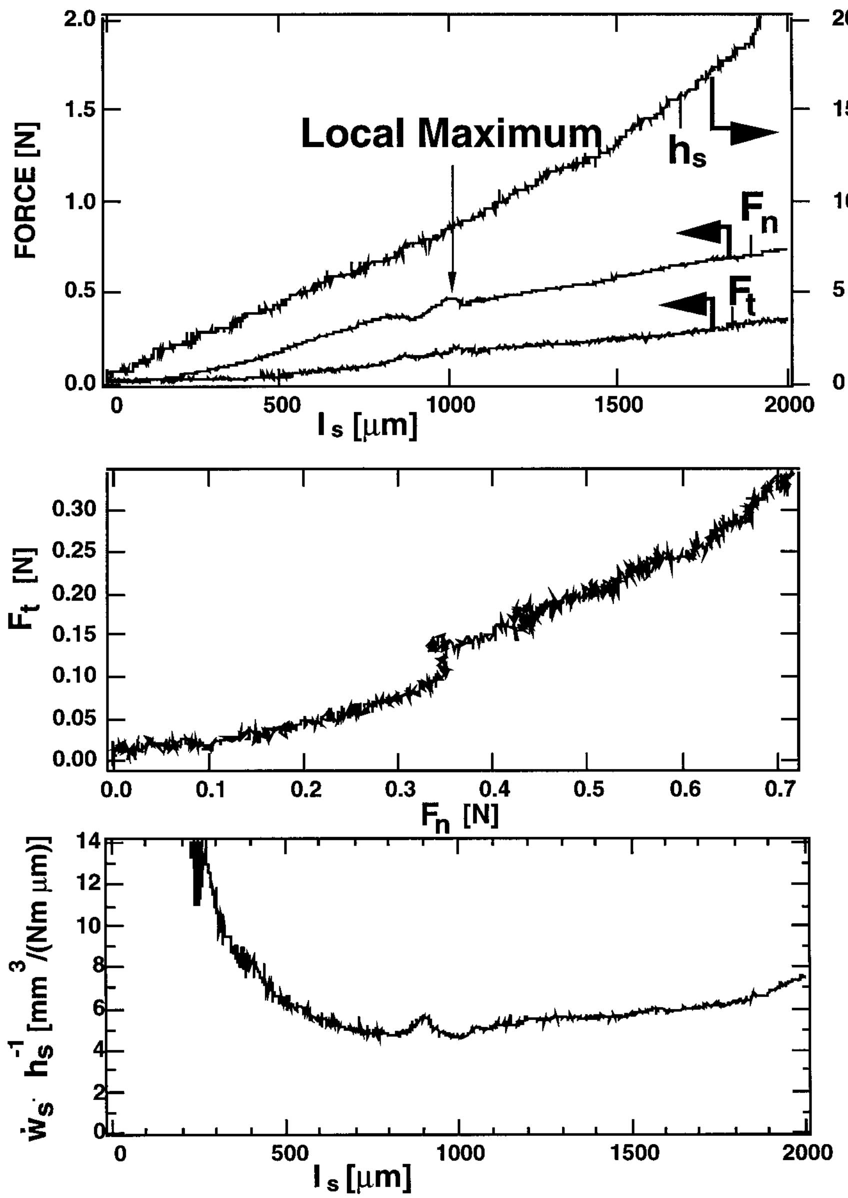
Sample Type/ Mold Temp (°C)	Avg H_r (μm)	ΔH_r (μm)	Avg H'_r (μm)	$\Delta H'_r$ (μm)	Avg H_{Vi} (kp mm^2)	ΔH_{Vi} (kp mm^2)	Avg H_t (μm)	ΔH_t (μm)	$c = H_r/H_t$
Skin/20	5.85	0.428	9.99	0.298	38.46	2.49	14.13	0.318	0.414
Bulk/20	4.95	0.238	9.57	0.031	42.07	0.20	13.80	0.137	0.359
Skin/80	5.81	0.311	10.13	0.404	37.49	2.90	14.41	0.369	0.403
Bulk/80	5.21	0.477	9.91	0.131	39.12	1.00	14.14	0.069	0.368
Skin/120	5.62	0.137	10.13	0.06	37.31	1.12	14.40	0.047	0.390
Bulk/120	5.66	0.386	10.23	0.331	36.81	2.38	14.97	0.359	0.378

The values of H_r, H_t, and H'_r should be considered as values of the slope shown in Figure 5. The values for ΔH_r, ΔH_t, and $\Delta H'_r$ are the standard deviations of the average values for each sample. H_{Vi} is the Vickers microhardness. The constant c that characterizes the viscoelastic behavior of the material is determined of all average values of H_r and H_t of each sample.



(a)

Figure 6 Results of scratch tests on the skin samples molded at (a) 20°C, (b) 80°C, and (c) 120°C and on the bulk samples molded at (d) 20°C, (e) 80°C, and (f) 120°C.

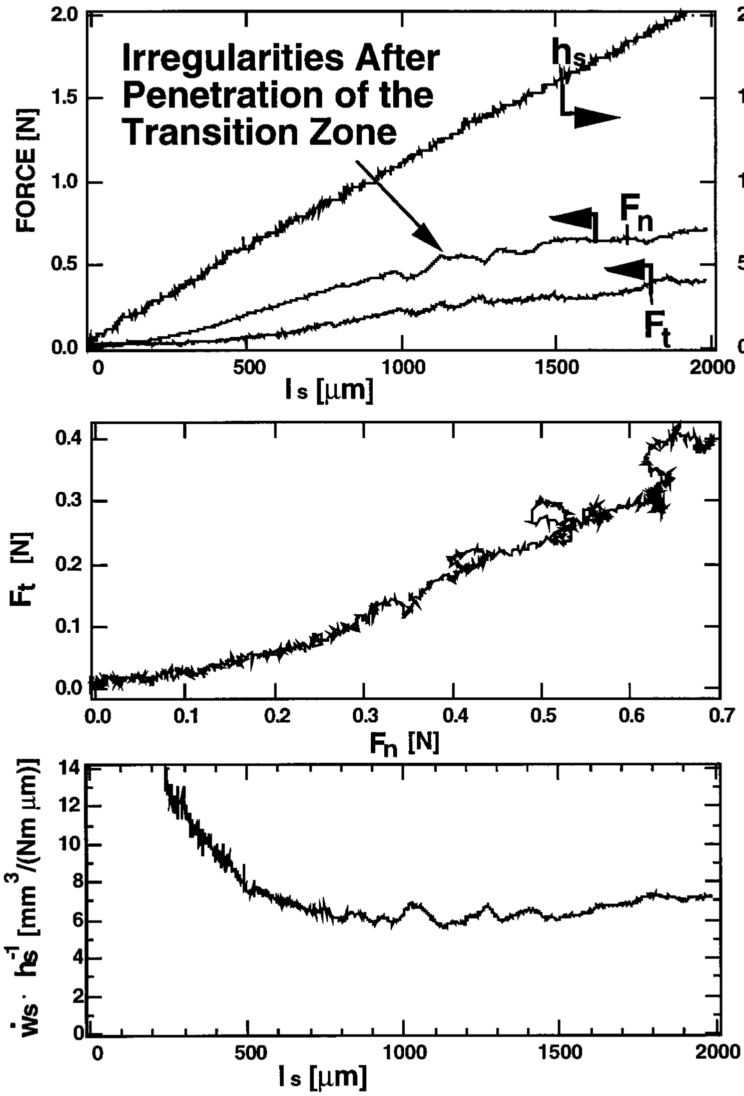


(b)

Figure 6 (*Continued from the previous page*).

EXPERIMENTAL

The equipment used for the tests is shown in Figure 3. The diamond indenter (an indenter of the shape that is shown in Figure 4 was used for the scratch tests) is fixed, and the tilted specimen moves beneath it. To start the test, the specimen is positioned as near as possible to the point of the indenter without touching the surface. This position is found by moving the indenter slowly (in 0.05-μm steps) toward the specimen and detecting the first signal from the normal load transducer beneath the specimen table. A typical load applied during this process is 0.01 N. The indenter moves a small distance away from the surface after it has detected the first signal, and this distance is taken into account during the indentation or scratch experiment. After starting the scratch, the time history of the normal force and the tangential force is measured with a piezoelectric transducer system. Simultaneously, the depth of the scratch is measured by an inductive displace-



(c)

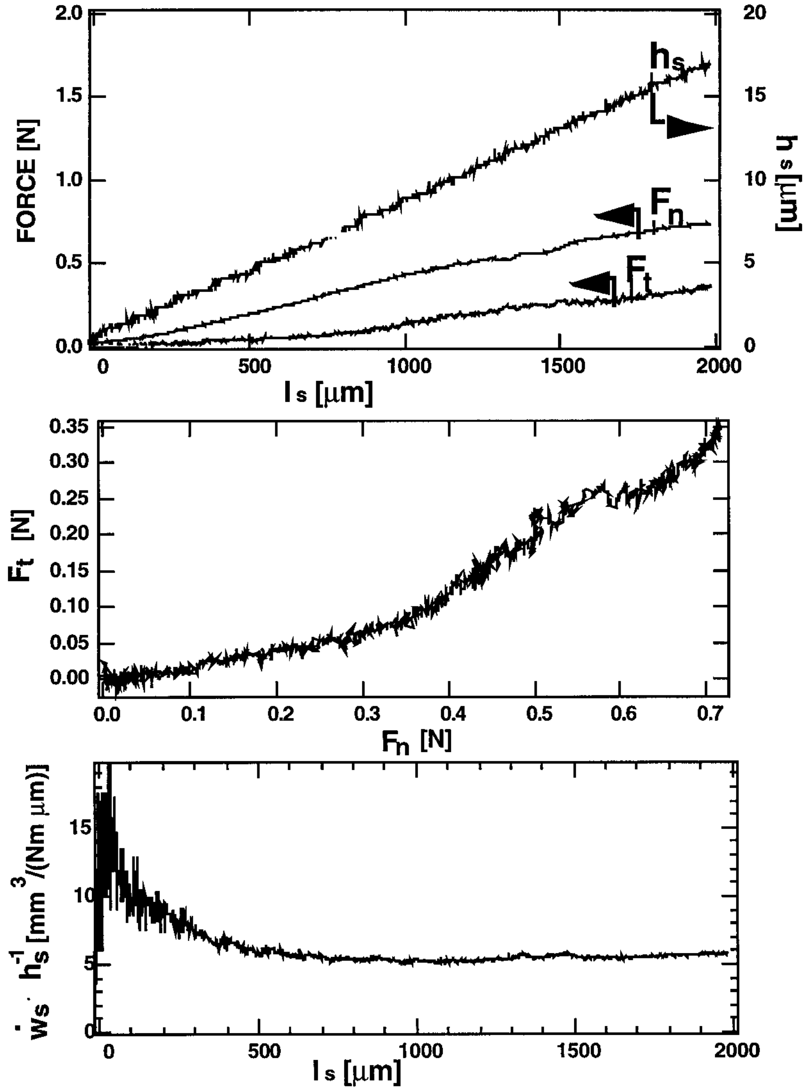
Figure 6 (*Continued from the previous page*)

ment transducer, which touches the specimen table. All measured data are amplified and recorded in ASCII format. After the test, an examination of the scratch is possible by the use of an optical microscope (Fig. 3).

For the indentation tests, a normal Vickers indenter was used. The indenter positioning procedure was similar to the one described above. The indentations were made on the same samples that were used for the scratch tests. A typical slope of the pressure versus depth during an indentation test is shown in Figure 5. All tests were made until the piezoelectric force transducer recorded a reaction force of 1 N. The average indentation time was in the range of 8–10 s. Since six indentations on the first sample (skin 20°C mold temperature) showed a Vickers microhardness in the range of 36–41 kp mm^2, it was considered that only three indentations on each of the other samples was sufficient to determine their microhardness quite accurately (see Table I).

RESULTS

Figure 6 shows the variation of the normal (F_n) and the tangential forces (F_t) during the scratches on



(d)

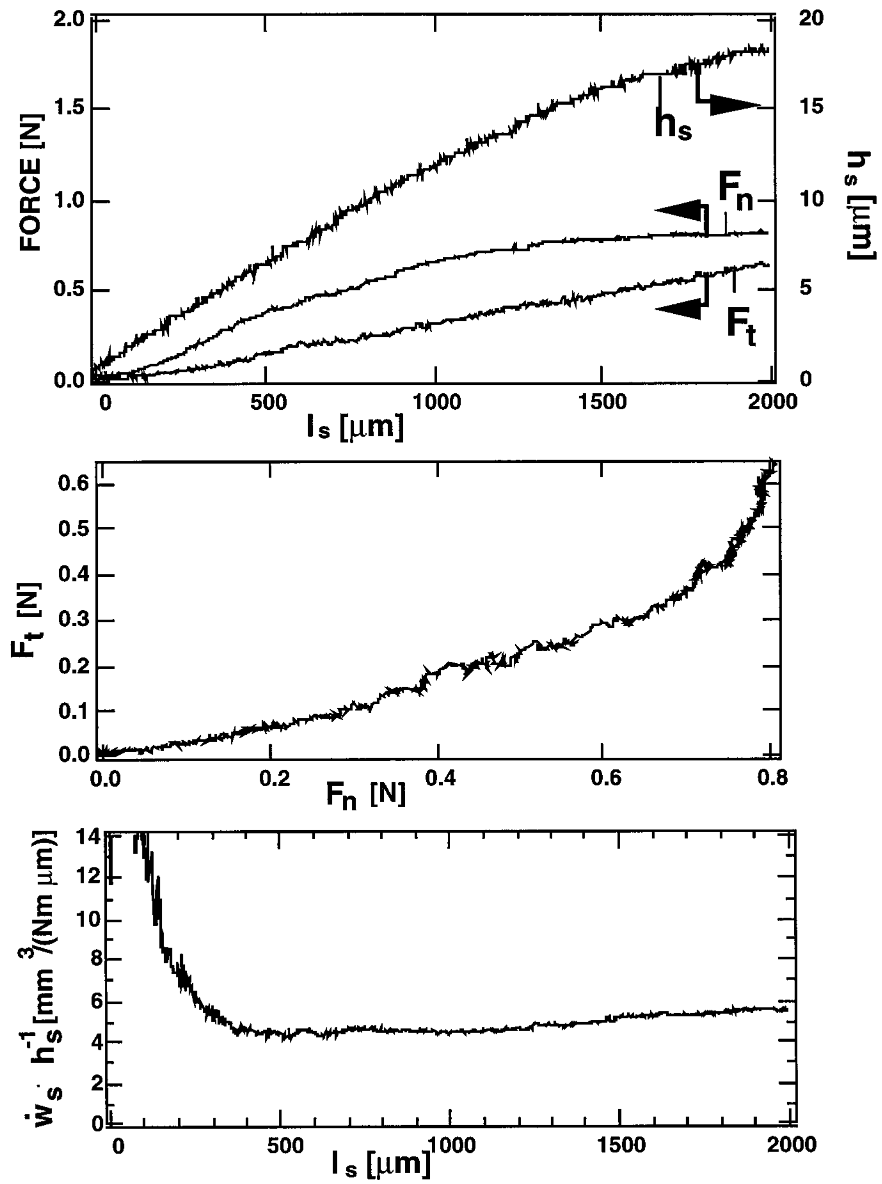
Figure 6 (*Continued from the previous page*)

the six different samples. The depth of the scratch (h_s), measured by displacement transducer, over the scratch length (l_s) is also displayed.

DISCUSSION

Scratch Tests

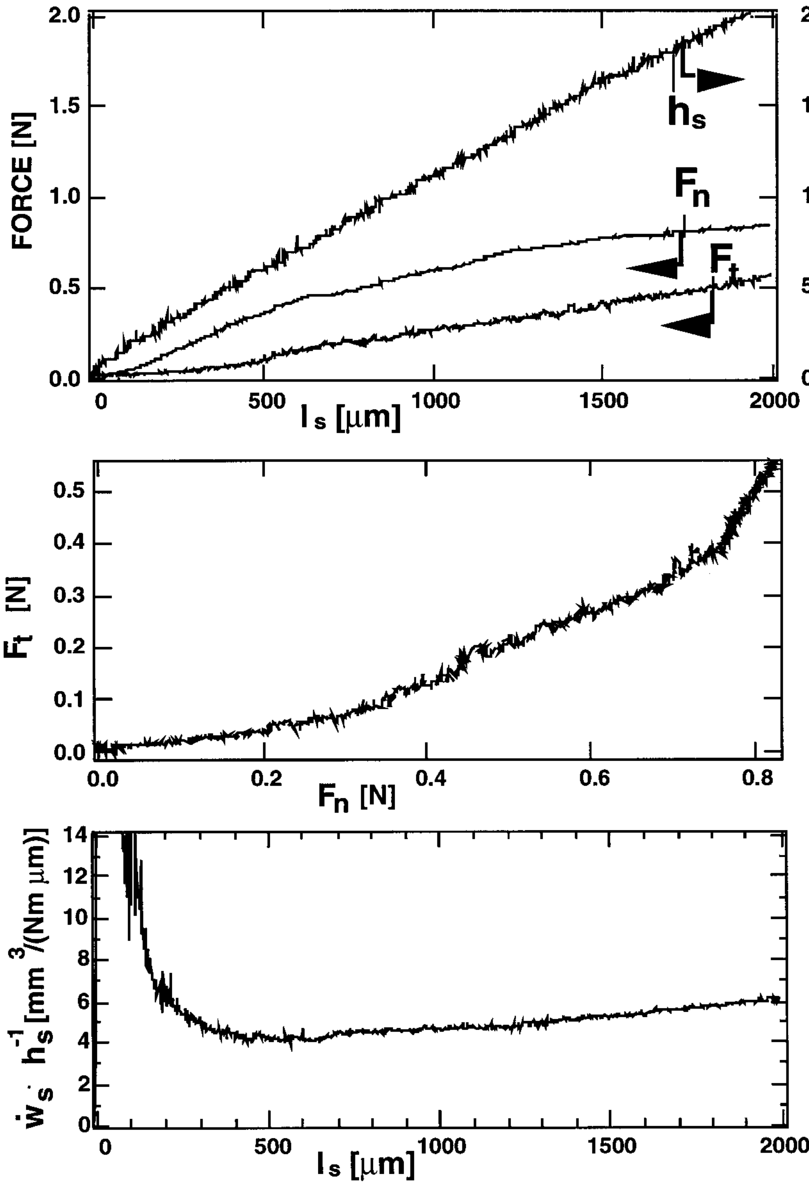
The slopes of the normal force of the scratches on the skin samples of 20 and 80°C [Fig. 6(a,b)] show sudden local maxima and minima at a scratch depth between 7.7 and 8.7 μm. The slope of the normal force of the scratch on the skin sample molded at 120°C is characterized by irregularities starting at a scratch depth of 10.7 μm [Fig. 6(c)]. The slopes of the normal force of the bulk samples [Fig. 6(d,f)], in comparison, are very smooth. The slope of the tangential force versus the normal force, i.e., the friction coefficient of the indenter and the specimen indicates this effect more obviously. Looking at the microtome cross sections [Fig. 2(a,b)] of both samples, one can assume that the local maxima occur due the breaking of the skin. The difference in thickness of the skin and the occurrence of the local maxima and minima in the slopes of the normal force is caused by the surface preparation (polishing with 1-μm diamond paste). Regarding the scratch on



(e)

Figure 6 (*Continued from previous page*)

the 120°C sample (where no skin is visible on the microtome cross sections), the local extrema of the normal force slope are due to the penetration of the transition zone. In other words, it is believed that after penetration of the transition layer, the indenter slides on the spherulitic bulk of the specimen and causes vibrations in the system due to the crystalline structure of this region. For this sample (skin at 120°C), the transition zone has a thickness of 11 μm [see Fig. 2(c)], corresponding to the first maximum of the normal force slope. Table II gives a survey of the thickness of skin and transition zone of each sample, along with the depth where the first irregularity in the normal force slope occurs. The reproducibility of this behavior has been verified by another set of scratches on the same samples. With regard to these results, the sudden appearance of local maxima and minima in the normal force slope reflects either the penetration of the skin or the penetration transition zone while scratching the surface of polyoxymethylene. The results of the indenta-



(f)

Figure 6 (*Continued from previous page*)

tion tests give no adequate explanation for this behavior. Therefore, it seems likely that the slope of the normal force is not affected by differences in hardness but by the orientation and shape of the crystals. The crystal orientation of DELRIN® is described in Böhme.[3] Figure 7 shows the different values of tangential force of skin and bulk samples for a fixed value of normal force. To characterize the abrasive wear resistance, it is possible to calculate a specific scratch–wear rate [eq. (1)]. Figure 8 shows the scratch system and the parameters that are used to determine the wear rate, as follows:

$$\dot{w}_s = \frac{c \cdot v_s}{F_n \cdot l_s} \left[\frac{\mathrm{mm}^3}{\mathrm{N\ m}}\right] \qquad (1)$$

where $c = \dfrac{H_r}{H_t}$ (see Table I) and H_r is measured residual penetration (value determined by indentation tests), H_t is penetration depth (value deter-

Table II Comparison of Morphology and Occurrence of Local Maxima and Minima

	At Mold Temperature of		
	20°C	80°C	120°C
Skin thickness (μm)	25	9.1	—
Transition zone thickness (μm)	254	196	11
Depth of scratch (on skin sample) where first local extrema in normal force slope occurs (μm)	7.7	8.7	10.7

mined by indentation tests), v_s is $l_s \cdot \tan 30° \cdot h_s$ = volume loss during scratch, F_n is normal force, l_s is length of scratch, and h_s is depth of scratch.

The slopes of the wear rates are related to the depth of the scratch h_s [see Fig. 6(a–f)] since the scratch was made at a certain angle; thus, the value of h_s varies. The ratio of the wear rate and h_s is nearly constant during the tests. The very high values in the beginning of the scratch are due to the fact that the displacement transducer that slides on the tilt table already records a depth of the scratch before the point of the indenter has deformed the first layer of the specimen. This represents, therefore, the sliding of the specimen over the surface without any indentation. The difference in wear resistance between the bulk and the skin samples (disregarding the local maxima and minima of the skin samples that were described above) of the three mold temperatures is negligible.The absolute values of the ratio of wear rate and scratch depth ($\dot{w}_s \cdot h_s^{-1}$) range between 4 and 6 $\times$ 10^{-6} mm^3 Nm $\times$ μm. However, it must be emphasized that in actual abrasion, abrasives and protuberances do not have edges as sharp as a diamond cone, and contacts occur at many points simultaneously. Thus, each abrasive does not scratch as effectively as shown in the single scratch system.[4] In fact, scratch hardness and wear rate values have to be considered as individual system properties; but, nevertheless, the determination of the scratch wear rate, especially for filled resins, can give the basis for a preliminary material choice.

Indentation Tests

The indentation test results show that the Vickers microhardness decreases slightly with increasing mold temperature (see Table I, Fig. 9). The skin samples molded at 20 and 80°C mold temperature show lower hardness than the bulk samples. The difference in hardness of the 120°C samples is very small. Compared to the microtome cuttings (Fig. 2), this demonstrates that the influence of the skin on the microhardness is detectable when the transparent zone has a certain thickness, i.e., the mold temperature is below 80°C. Figure 10 shows this dependence as a straight line relationship. A comparison of both testing methods (scratch and indentation) shows that the dynamic, continuous, and oriented movement of the scratch indenter permits more detailed observation of the viscoelastic behavior of the material and its resistance against abrasive wear mechanisms than standard indentation or microhardness tests. Moreover, scratch testing seems to be a good tool to study effects of crystallinity on the scratch resistance of certain materials. The results of the scratch tests herein show that the resistance of the material to the sliding movement of the indenter varies at different depths of the sample. The assumption that the crystallinity is responsible for the recorded peaks in the normal force slopes could be based, therefore, on the model of different intercrystalline bonding forces in the different zones. Adhesion forces between the indenter and crystals can play a role too. However, this phenomenon has to be further explored, and an analysis of the intercrystalline bonding

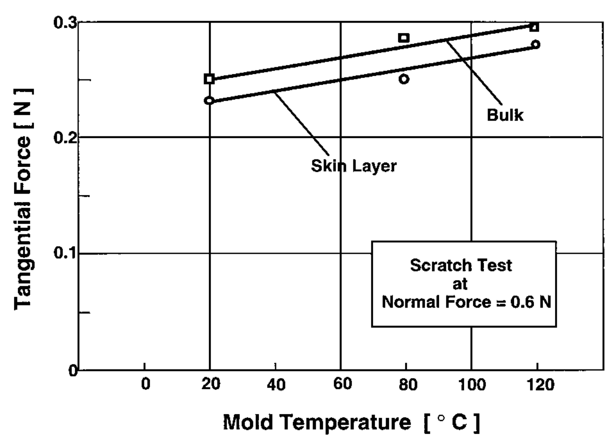


Figure 7 Effect of mold temperature on tangential force during scratch test of POM materials.

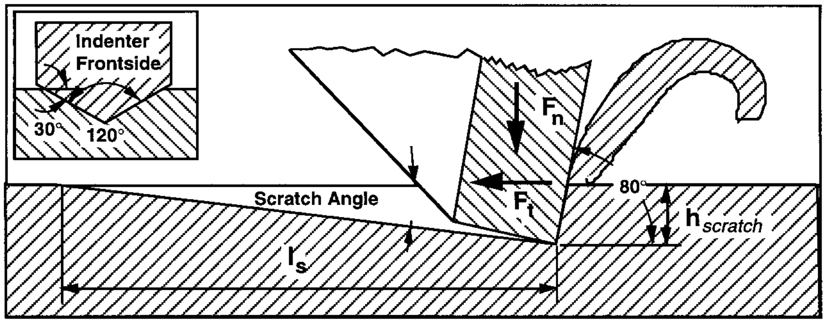


Figure 8 Geometry of scratch system.

forces in the different zones should give more information about the actual conditions.

CONCLUSIONS

1. The effect of the skin of polyoxymethylene is detectable when scratch tests on bulk and on skin samples are compared. In this case, the piercing of the skin leads to local maxima and minima of the normal force slope (during scratching).
2. The mold temperature does not affect the microhardness of the skin. A difference in microhardness of the bulk and the skin is detectable at low mold temperatures. In this case, the bulk shows higher microhardness values than the skin.
3. An increase in mold temperature that normally leads to an increase of elongation at break values[5] does not visibly effect the microhardness of polyoxymethylene.
4. The different scratch behavior of the skin and bulk samples is not necessarily due to the microhardness but possibly due to the molecular orientation of the crystals in the different zones of the samples. An analysis of this phenomenon should take into account the intercrystalline bonding forces in the different zones of molecular orientation.
5. Scratch testing seems to be a good tool to characterize the abrasive wear resistance

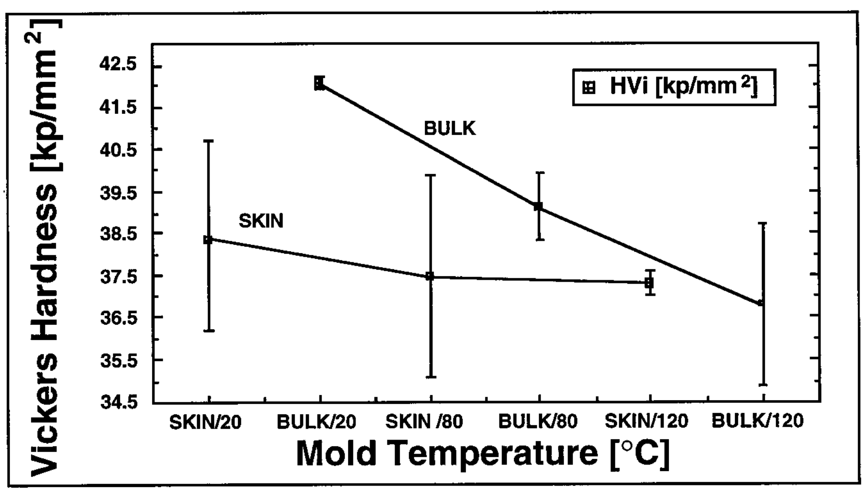


Figure 9 Microhardness of DELRIN® 100 of different mold temperatures. The results of the indentation tests show that an effect of mold temperature on the microhardness is not well pronounced. There is however a small difference in microhardness detectable betwee the two different crystallization zones (skin and bulk) especially for the low mold temperature samples.

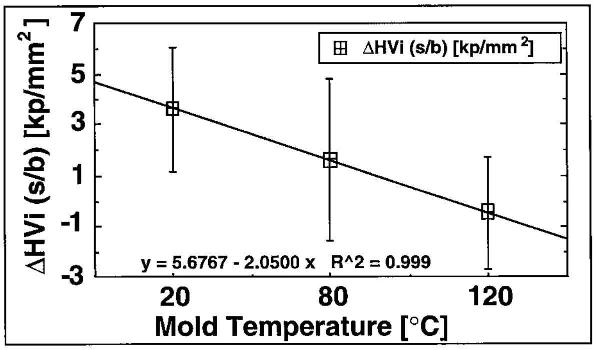


Figure 10 Straight line relation between difference in hardness of skin and bulk samples of DELRIN® 100 and their mold temperature.

of materials. Linking the values gained in these experiments to abrasion tests on the same material can be a future task. Scratch testing is much more efficient, but the difference of the tribological system must always to be kept in mind. The time that is needed to make a single scratch is less than the time that an abrasion test takes. Also, the damage of the surface region during abrasion tests (e.g., on a taber abrader) after some testing time influences the further wear progress.

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