# Characterization of Mold Fouling During Elastomer Injection Molding

Peter R. Hornsby,[1] Inderjeet Singh,[2] John R. Daley,[3] John Firth[3]

[1]School of Mechanical and Aerospace Engineering, Queen's University, Belfast, BT9 5AH, United Kingdom
[2]Wolfson Centre for Materials Processing, Brunel University, Uxbridge, Middlesex, UB8 3PH, United Kingdom
[3]Trelleborg Sealing Solutions, Limited, Ashchurch, Tewkesbury, Gloucestershire GL20 8JS, United Kingdom

**ABSTRACT:** Consideration is given to the characterization and origins of mold fouling occurring during the injection molding of elastomers. Results for nitrile rubber and fluoroelastomer compounds are presented with a range of techniques, including light microscopy, scanning electron microscopy, elemental analysis by energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and surface-energy measurements with the sessile drop approach. A specially designed mold tool combined with interchangeable cavity inserts has also enabled the exploration of the effects of different metal surface treatments on the onset and extent of mold fouling. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3186–3194, 2006

**Key words:** molding; rubber; surfaces

## INTRODUCTION

The phenomenon of mold fouling commonly occurs when elastomer products are injection-molded. In this process, rubber, usually in a precompounded form, is rapidly transferred from a warm injection cylinder to a hot mold, in which the material crosslinks by a vulcanization process. At the end of this curing stage and after the removal of the molding, a thin deposit of the material can remain on the mold surface and progressively builds up with repeated injection cycles. The magnitude of this effect critically depends on a number of factors, including the chemical nature of the rubber compound, the mold surface composition, the quality of the finish, and the injection-molding conditions.

The presence of a rubber-deposit layer on a mold has significant commercial implications because it impedes heat transfer from the mold to the polymer, is the source of mold-release problems, and can create defects on the molding surface. Furthermore, mold fouling results in material wastage, requires regular cleaning of the mold, and generally necessitates the use of mold surface treatments, all of which add to production costs. The most common temporary solution used to limit fouling is to spray the mold with a release agent at regular intervals, although elastomer compounds can be formulated with inherently superior mold-release characteristics.

Despite the extensive range of injection-molded rubber products produced commercially and the resulting costs of mold fouling to industry, a detailed understanding of the origins of this phenomenon has not been elucidated. To this end, the results reported in this communication form part of a wider investigation to systematically examine the origins of mold fouling with nitrile and fluoroelastomer polymer compounds injection-molded into mold cavities differing in the surface composition and texture. Full technological details arising from this study are given elsewhere.[1] However, this article focuses on the methods used to characterize the surfaces of molds with different surface modifications, before and after fouling has occurred, to provide a basis for more fully understanding the causes of this effect.

## EXPERIMENTAL

### Materials

Two commercial elastomer formulations were studied, both supplied in strip compound form by Trelleborg Sealing Solutions, Ltd.: a nitrile rubber (NBR) and a fluoroelastomer (FKM). These were chosen because industrial experience had shown that these materials experienced some level of mold fouling.

### Injection molding

Cylindrical moldings (22 mm long and 10 mm in diameter) were produced from these materials with a Dr Boy 30M horizontal injection-molding machine (Germany) and specially designed tooling (Fig. 1) that
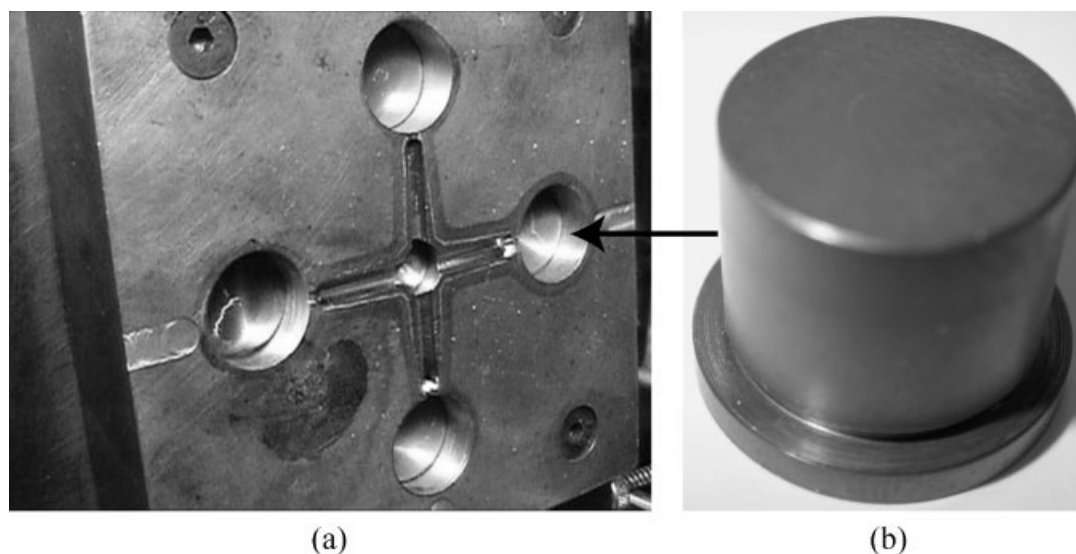
**Figure 1** (a) Injection mold cavity and (b) replaceable insert.

allowed interchangeable inserts to be incorporated into the cavity, so that the effects on mold fouling against different surfaces could be studied. For this purpose, Stavax mold inserts with and without surface treatments were used. Stavax ESR steel has the following elemental composition, the balance being iron: 0.38 wt % carbon, 0.9 wt % silicon, 0.5 wt % manganese, 13.6 wt % chromium, and 0.3 wt % vanadium. In this article, coatings made from a polytetrafluoroethylene (PTFE)-containing material, titanium nitride (TiN), and chromium and diamond-like coatings are specifically mentioned. Further details on these and their method of preparation can be found elsewhere.[1]

Test samples from nitrile and fluoroelastomer compounds were prepared with increasing numbers of molding cycles under the processing conditions shown in Table I.

### Surface characterization procedures

The surfaces of the molds and corresponding moldings were analyzed to provide information about the location and onset of mold fouling, the chemical origin of these deposits, the changes to the surface energy of molds after repeated molding, and the nature of the mold, with and without surface treatment. For this purpose, the following techniques were employed to study the surfaces of the mold inserts and in some cases moldings.

### Visual inspection and light microscopy

In many instances, the direct observation of moldings revealed the presence of surface changes as a result of mold fouling, which could also be apparent on the mold surface after repeated molding. Generally, however, these surface deposits were more clearly seen by reflected light microscopy with incident light at a low magnification.

### Scanning electron microscopy (SEM)/energy-dispersive X-ray (EDX) spectroscopy analysis

The surface textures and chemical compositions of the molds and moldings were determined by SEM with a JEOL 840A instrument combined with EDX spectroscopy at 20 kV, which incorporated PGT-$\gamma$ software. An EDX line-scan technique was used to quantify the elemental composition along a given profile and within a specified field of view. In most cases, the rubber samples were sputter-coated with gold to reduce surface charging.

### X-ray photoelectron spectroscopy (XPS)

XPS was used to detect changes in the chemical composition at the mold surfaces before and after molding with an ESCA VG Escalab 210 instrument. The peaks were recorded as a function of the binding energy,

**TABLE I**
**Injection-Molding Conditions for the NBR and FKM Compounds**

| | Barrel temperature (°C) | Vulcanization temperature (°C) | Vulcanization time (s) | Injection time (s) | Injection pressure (bar) | Holding pressure (bar) |
|---|---|---|---|---|---|---|
| NBR | 65 | 165 | 120 | 6 | 138 | 65 |
| FKM | 80 | 185 | 90 | 5 | 145 | 85 |

from which the peak compositions were determined. The analyzed chemical elements included carbon, oxygen, and fluorine. The proportions of these elements were estimated by a comparison of the C1s, O1s, and F1s peak areas obtained from the differential cross sections for core-level excitation. All XPS measurements were made at an electron takeoff angle of $40°$, which corresponded to an attenuation length of $\sim 5.0$ nm.[2]

## Surface-energy and contact-angle measurements

A sessile drop method was used to measure the surface energies and contact angles of the mold cavity surfaces. This was undertaken with a purpose-built test rig comprising a horizontal, long-focusing microscope and a combined goniometer (Fig. 2). A graticule eyepiece was positioned at the boundary of the drop, magnified 12 times, and rotated to make a line at the tangent to the drop. The extent of rotation measured by the goniometer was used to determine the contact angle to an accuracy of $\pm 1°$. The surface energies of fresh and fouled mold inserts were determined by this method with water (polar) and methylene iodide (nonpolar) of a known surface energy as the probe media.[3] The surface energy of the mold inserts was calculated with the Young–Dupré expression.[4] Measurements were taken on each side of the droplet, and the test was repeated in triplicate for each mold insert. The drop shapes were strongly influenced by the mold surface treatment applied (Fig. 2).

## Surface roughness

The surface roughness of the Stavax mold inserts was measured with a Talysurf series 2 profilometer. The surface roughness was defined as the average value of the distance from the surface to a center reference line[5] and was calculated by the summation of the deviations from the centerline and division by the number of data points along a selected 100-μm length. Twenty-five points per micrometer were used, yielding a total of 2000 data points for the determination of a single roughness value. Each sample was scanned in 25 randomly selected locations.

## RESULTS AND DISCUSSION

### Studies using the nitrile rubber compound

A visual inspection showed that mold fouling occurred at different positions on the cavity inserts and after different numbers of cycles according to the nature of the
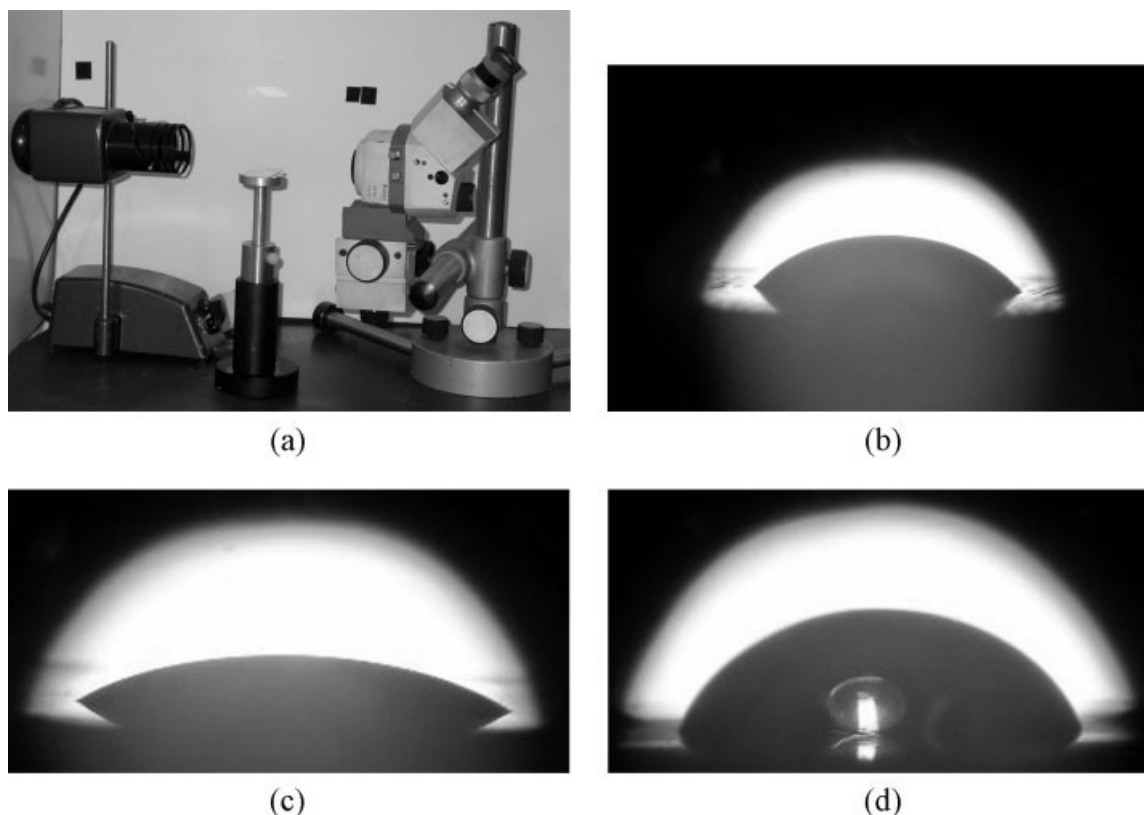


**Figure 2** Measurement of the surface energy on uncoated and surface-treated Stavax mold inserts: (a) apparatus for sessile drop measurements, (b) TiN coating with water, (c) untreated Stavax with water, and (d) diamond-like coating with methylene iodide.

mold surface. For example, with NBR, marks on the molds and rubber moldings were first apparent after 40 cycles for the uncoated Stavax mold surface, after 20 cycles for the Stavax mold coated with a PTFE-containing composition, and after 167 cycles for the Stavax mold coated with TiN. However, an initial deposit layer is likely to have occurred much earlier than this, possibly even after the first shot, but the rate of buildup was clearly dependent on the mold surface composition. As mold adhesion became more significant with repeated cycling, the effects on the molding quality were more evident. As shown in Figure 3, initially this may have resulted in a slight change in the molding appearance, which progressively increased in intensity to the point at which ejection from the cavity was impaired; this caused tearing and damage to the molding surface. Corresponding rubber deposition on the cavity surface occurred, and this was apparent with light microscopy or, in the case of the fluoroelastomer, with the naked eye (Fig. 3).

The incidence of mold fouling depends on the quality and composition of the mold surface, in addition to chemical changes occurring as the rubber is molded, the processing conditions applied, and the location and design of the cavity gating used. These aspects have been considered elsewhere in systematic molding trials and mold-filling simulation studies.[6]

Untreated Stavax mold surface

Figure 4 shows the irregular surface texture of the untreated Stavax mold insert before the commencement of molding.
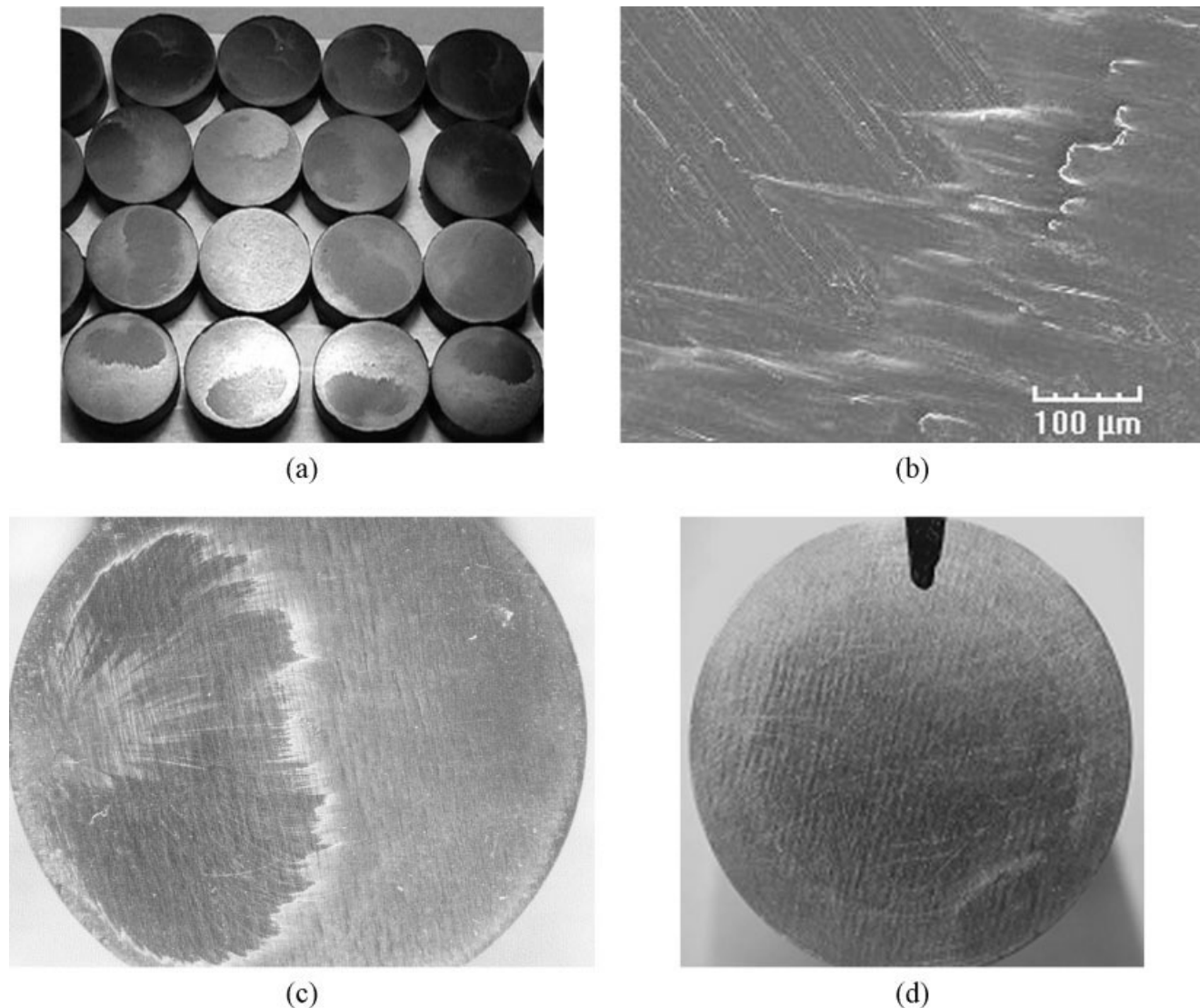


**Figure 3** Effects of mold fouling: (a) surface of nitrile rubber moldings, (b) tearing of nitrile rubber on the surface of a molding (scanning electron micrograph), (c) Stavax mold insert with a nitrile rubber deposit (reflected light micrograph), and (d) Stavax mold insert with a fluoroelastomer deposit.
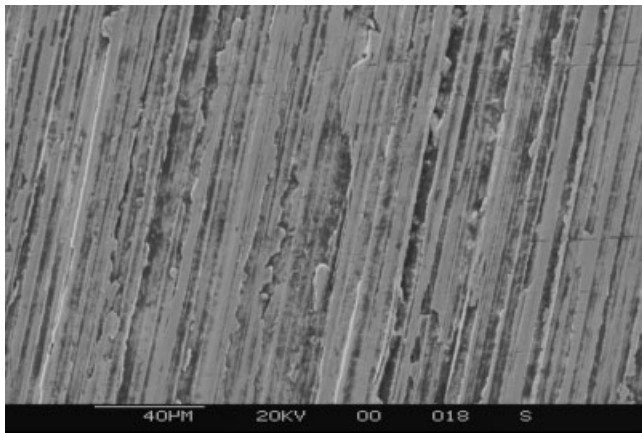
**Figure 4** SEM micrograph of an untreated Stavax mold before molding.

Backscattered images of this untreated Stavax mold surface after 700 successive moldings are shown with increasing magnification in Figure 5, in which the rubber-deposit layer is clearly visible. To identify the interface location for the deposit layer on the mold insert and to explore the elemental composition across this surface, SEM coupled with an EDX line scan was applied [Fig. 5(c)]. A line scan 130 μm long, at 200× magnification, was selected across the rubber-deposit interface.
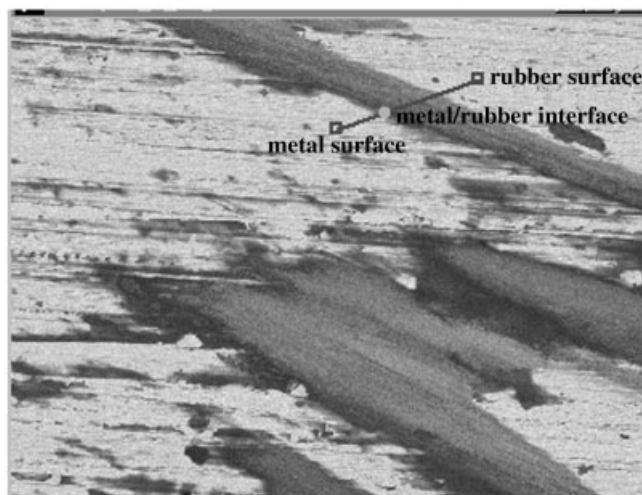
The elemental concentration was analyzed at three different positions: at the metal surface away from the fouled area, at the rubber-rich surface, and at the rubber-deposit/metal interface. The sharp increase in the concentrations of carbon, zinc, calcium, and sulfur at the deposit interface, as shown in Table II,
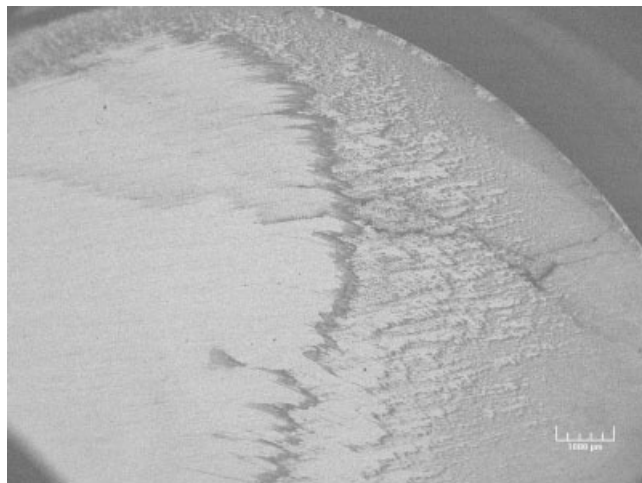


(a)
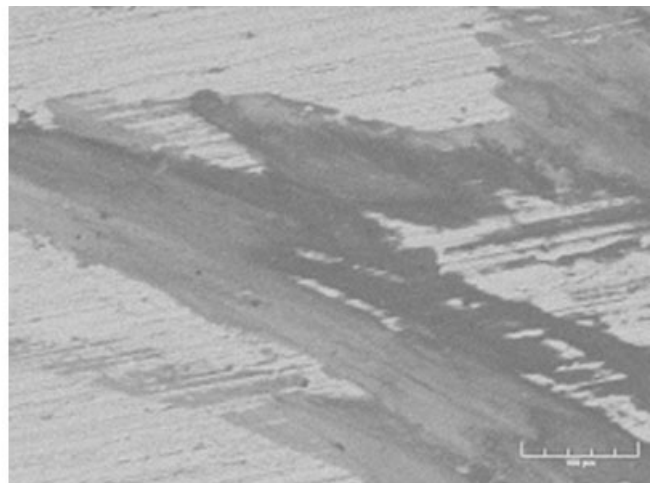


(b)



(c)

**Figure 5** (a) Backscattered SEM image of an uncoated Stavax mold after 700 moldings at the nitrile rubber deposit interface, showing the region taken for sample analysis; (b) magnification of the region identified in part a; and (c) location of the EDX line scan in the rubber-rich region, at the rubber-deposit/metal interface, and at the metal surface.

**TABLE II**
**Elemental Analysis of the Uncoated Stavax**
**Mold Surface after 700 Moldings[a]**

| Element | Concentration (wt %) | | |
| --- | --- | --- | --- |
| | In the rubber region | At the interface | At the metal surface |
| Carbon | 2.2 | 2.1 | 1.4 |
| Oxygen | 3.8 | 3.1 | 1.4 |
| Sulfur | 34.3 | 26.1 | 8.7 |
| Calcium | 20.0 | 18.0 | 5.0 |
| Zinc | 15.4 | 5.0 | 2.1 |
| Silicon | 7.0 | 9.6 | 6.0 |
| Chromium | 10.4 | 27.6 | 43.8 |
| Potassium | 6.9 | 8.6 | 5.0 |
| Iron | — | — | 27.0 |

[a] From the line scan in Figure 5.

confirmed the starting point for the layer of the rubber deposit, although the presence of traceable amounts of carbon, zinc, and sulfur away from the rubber-rich zone indicated that there was also a thin layer of rubber on the metal cavity surface. The highest concentrations of carbon, zinc, calcium, and sulfur were found in the thicker mold deposit layer.

EDX elemental analysis data across the mold deposit also showed that the formation of this layer correlated with an increase in the oxygen concentration across the interface zone. The oxygen found in the mold deposit surface might be associated with the deposition of a zinc oxide additive and/or reactions with the rubber resulting from oxygen present in the cavity during the molding cycle. The concentrations of other elements listed in Table II indicate
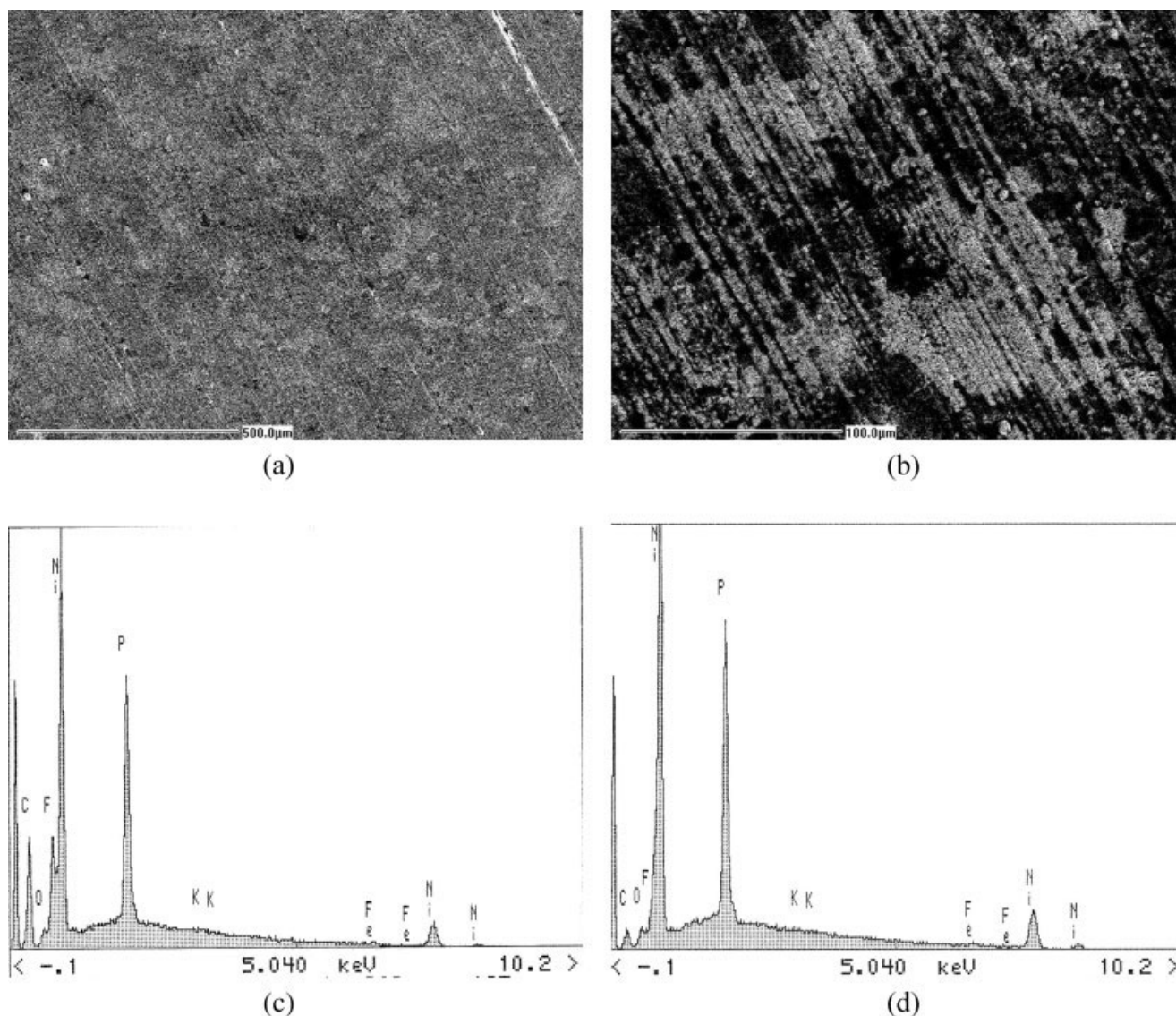


**Figure 6** (a,b) SEM backscattered images of a Stavax mold with a PTFE-containing coating, (c) EDX spectrum of the black region, and (d) EDX spectrum of the white region.
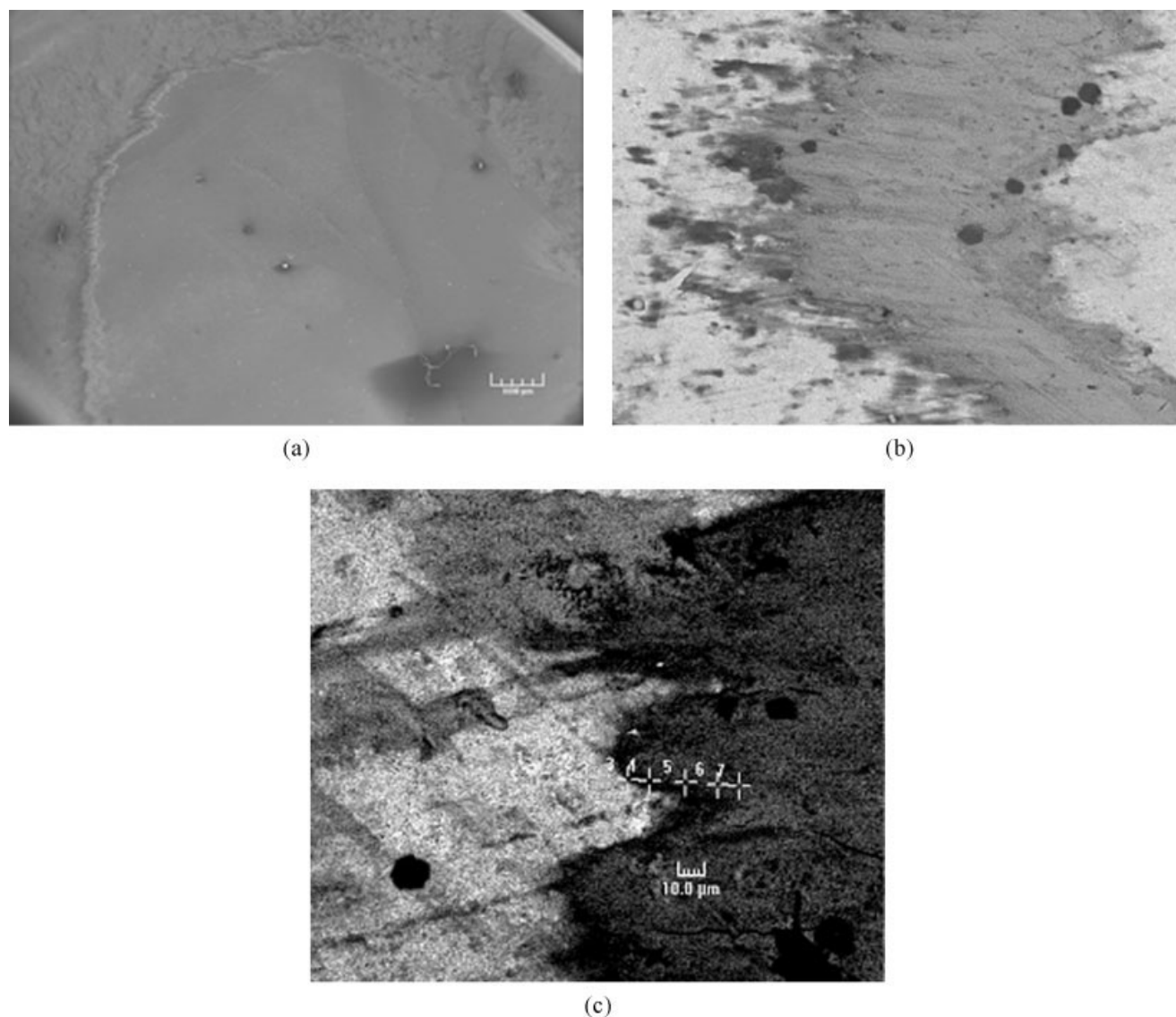
**Figure 7** (a) SEM micrograph of a Stavax mold with a PTFE-containing-coating insert after 320 nitrile rubber moldings, showing the position taken for analysis; (b) higher magnification of the selected region in part a; and (c) position of the EDX line scan.

that the zinc content in the deposit layer increased 7 times in comparison with zinc at the metal surface. Moreover, after only limited molding, there was much more migration of sulfur than zinc onto the mold surface. It is also possible that the zinc oxide reacted with the sulfur to form zinc sulfide, creating an insoluble inorganic deposit, although this has not been substantiated.

**TABLE III**
**Elemental Concentrations (wt %) at Different Positions in an SEM Micrograph[a]**

| Tag | Carbon | Oxygen | Fluorine | Phosphorus | Nickel | Silicon | Sulfur | Zinc | Carbon | Iron |
|-----|--------|--------|----------|------------|--------|---------|--------|-------|--------|------|
| 1 | 26.82 | 0.86 | 0.0 | 14.88 | 53.87 | 0.16 | 0.75 | 1.06 | 0.23 | 1.36 |
| 2 | 26.81 | 1.07 | 0.0 | 12.39 | 56.94 | 0.21 | 0.91 | 0.06 | 0.22 | 1.39 |
| 3 | 33.53 | 1.43 | 0.0 | 11.69 | 48.12 | 0.22 | 1.12 | 2.50 | 0.24 | 1.15 |
| 4 | 32.02 | 4.20 | 0.04 | 6.74 | 33.35 | 0.58 | 3.12 | 17.53 | 1.44 | 0.98 |
| 5 | 29.99 | 7.44 | 0.0 | 0.54 | 5.82 | 1.04 | 6.20 | 43.99 | 4.42 | 0.56 |
| 6 | 38.42 | 5.52 | 0.61 | 0.17 | 3.73 | 1.18 | 4.41 | 42.29 | 3.23 | 0.45 |
| 7 | 31.37 | 6.72 | 0.0 | 0.11 | 3.91 | 1.65 | 4.63 | 47.84 | 3.29 | 0.47 |

[a] See Figure 7.

TABLE IV
Surface Roughness and Energy Values of Various Mold Surfaces

| Stavax coating | Surface roughness (μm) | Surface energy (N/m) | Onset of mold fouling (cycles) |
|---|---|---|---|
| Uncoated | — | 0.12 | 40 nitrile |
| TiN | 0.221 | 0.036 | 167 nitrile |
| PTFE-containing | 0.20 | 0.05 | 20 nitrile |
| Uncoated | — | 0.12 | 5–10 fluoroelastomer |
| Diamond-like | 0.047 | 0.04 | >1500 fluoroelastomer |
| Chromium | — | 0.08 | 150 fluoroelastomer |
| TiN (after 350 moldings)[a] | 0.264 | — | — |
| PTFE-containing (after 350 moldings)[a] | 0.23 | — | — |

[a] With a fluoroelastomer compound.

**Stavax mold with the PTFE-containing coating**

Figure 6(a,b) shows SEM micrographs of uncontaminated Stavax mold inserts with PTFE-containing coatings, indicating a rough surface texture and a lack of coating uniformity. EDX spectra measured in the black and white regions are compared in Figure 6(c,d). Although the overall compositions appeared the same, there were apparent differences in the relative peak heights for carbon, fluorine, phosphorus, and oxygen in these regions, which reflected variations in the coating concentration due to imperfections in the surface-treatment process.

Figure 7 shows backscattered images from this mold insert after 320 consecutive moldings, revealing a substantial layer of rubber deposited across the surface. A seven-point EDX line scan was undertaken across the boundary between the metal and rubber regions. Table III shows the differences in the elemental concentration (wt %) at these positions. The EDX results showed a progressive reduction of nickel and phosphorus (present in the mold surface coating), with corresponding increases in the concentrations of zinc,

sulfur, and calcium, which were related to the onset of mold fouling. It is possible that the reaction of zinc and sulfur with nickel on the mold surface produced fouling, although this remains speculation. As with the uncoated Stavax, it is significant that the amount of oxygen detected also increased with progressive mold fouling. The low concentrations of fluorine detected were attributed to the lack of coating uniformity.

**Studies using a fluoroelastomer compound**

Surface-energy and surface-roughness measurements

The surface energy of a material can be influenced by a number of factors, including its chemical composition, surface charge, and microstructural topography. However, the relationship between these surface properties is not always clear, nor is the correlation of the surface energy with the tendency for elastomers to foul injection molds.

The surface energies of all the coated molds were significantly lower than those for untreated Stavax, with the lowest values observed for TiN and dia-



(a)

(b)
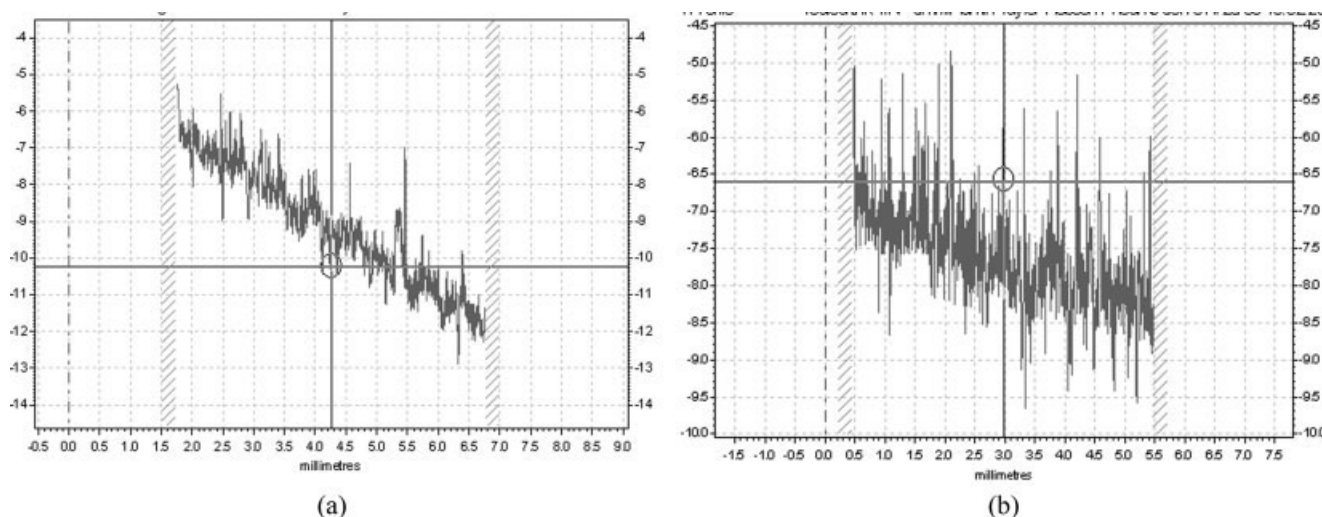
**Figure 8** Surface-roughness profiles for a TiN-coated Stavax mold: (a) before molding and (b) the mold fouled with a fluoroelastomer.

**TABLE V**
**Elemental Concentrations Determined by XPS for a TiN-Coated Stavax Mold Before and After Molding with a Fluoroelastomer Compound**

| Element | After 350 moldings (atom %) | Before molding (atom %) |
|---|---|---|
| Carbon | 78.3 | 34.2 |
| Oxygen | 9.4 | 26.0 |
| Nickel | 2.4 | 12.8 |
| Titanium | 4.1 | 27.0 |
| Fluorine | 5.9 | None |
| O1s/C1s | 0.1 | 0.7 |

mond-like coatings indicating their greater hydrophobicity (Table IV). Typical sessile drops of water and methylene iodide on these surfaces are shown in Figure 2. Surface-roughness measurements for coated mold variants were very similar, except for the diamond-like coating, which was significantly smoother (Table IV). Measurements undertaken after 350 moldings show increased roughness (Fig. 8), reflecting the presence of the rubber deposit. The slope of these curves resulted from the fact that the measured surfaces were not flat. It is notable, however, that the onset of mold fouling was significantly delayed with the chromium and diamond-like surface coatings, although it is not clear whether this was due to a surface-energy effect, reduced roughness, or a combination of both.

XPS analysis of the mold surfaces

XPS was used to detect changes in the chemical composition in an approximately 5.0-nm-thick layer at the insert surface after repeated molding had occurred. A curve-fitting technique was employed to find the individual chemical states from the spectrum of each element. To compensate for charging, the binding energy (BE) was calibrated, with the C1s of the principal carbon peak fixed at 285 eV as an internal reference.

Table V shows the elemental concentration on TiN-coated Stavax before molding and after repeated cycling with a fluoroelastomer compound. These results reveal that the amounts of titanium and nickel decreased as the amounts of carbon and fluorine increased, reflecting the presence of the fluorocarbon mold deposit on the coating surface. There was also a significant decrease in oxygen in the fouled molding. This was in contrast to the situation with the nitrile rubber compound; having a totally different formulation, as mentioned earlier, it showed an increase in the oxygen present in the rubber deposits.

## CONCLUSIONS

Observations of nitrile rubber and fluoroelastomer mold fouling during injection molding have been presented. A visual inspection and reflected light microscopy have revealed changes in the surface texture and appearance of both the mold and molding surfaces. SEM combined with EDX has provided quantitative information about the nature of these mold deposits, including the presence of compounds originating from the processed rubber. The role of oxygen in mold fouling, particularly in the case of nitrile rubber, has also been highlighted. Complementary chemical information has been given by XPS in the first few nanometers of the mold surface. In comparison with the control Stavax steel mold surface, modifications with PTFE-containing, TiN, chromium, and diamond-like coatings have caused a significant reduction in the surface energy and a corresponding delay in the onset of mold fouling upon repeated molding.

## References

1. Singh, I. Ph.D. Thesis, Brunel University, UK, 2005.
2. Seah, M. S.; Dench, W. A. Surf Interface Anal 1979, 1, 2.
3. Fowkes, F. M. J Phys Chem 1962, 66, 382.
4. Young, T. Philos Trans R Soc 1805, 95, 65.
5. Hallab, N.; Bundy, K.; O'Connor, K.; Clark, R.; Moses, R. L. Proceedings of the 14th Southern Biomedical Engineering Conference, Shreveport, LA, 1995; p 81.
6. Hornsby, P. R.; Singh, I.; Daley, J. R.; Firth, J. In Proceedings from Polymer Process Engineering '05, University of Bradford, Bradford, UK, July 5, 2005; Coates, P. D., Ed.; p 208.