

External Lubrication of High-Temperature Thermoplastic Polymers

T. A. STOLARSKI

Department of Mechanical Engineering, Brunel University, Uxbridge, Middlesex, UB8 3PH, United Kingdom

SYNOPSIS

External lubrication of high-temperature thermoplastic polymers was studied experimentally. It was found that the nature of the lubricating fluid has a pronounced effect upon the behavior of the contact. It is postulated that premature failure of PEEK-lubricated contacts is caused by the migration of linear carboxylic acids into the polymer matrix at elevated temperatures, thereby producing significant plasticization. A sequence of events leading to failure is given and some rationale for it provided. © 1993 John Wiley & Sons, Inc.

1. INTRODUCTION

Polymers are usually perceived as materials that do not require any external lubrication to secure low friction. The truth of the matter is somewhat different from this conventional view, as some of them, namely, high-temperature thermoplastics, require external lubrication to function as a material of sliding contact. Significant improvement in contact performance may often be obtained by conventional liquid lubrication, but a number of subtle interfacial phenomena are sometimes observed, some of which are deleterious to good operation.

A number of studies on the influence on polymer friction of adsorbed molecules of conventional boundary lubricants—long-chain paraffins, alcohols, esters, acids, etc.—have been carried out.^{1,2} In general, it was found that the effectiveness of lubrication of different molecular types ranked in the same order for polymers as for metals. The actual reductions in friction achieved, however, were much less. The latter result is partly because it is difficult to form close-packed, adsorbed monolayers on some polymers and partly because the shear strengths of such monolayers are not, in any case, very different from those of many polymers. It was also found that the lower the solubility parameter the more effective, in general, is the fluid in its lubricating role. The solubility parameter alone is hardly likely to be primarily re-

sponsible and it is more plausible to look for some other factor that is closely correlated with it. Surface tension is one such factor. There is much confusion in the literature about the role of surface tension and wettability in the lubrication of polymers. Specific instances have been reported^{3,4} of reductions in friction when the surface tension of the lubricant is reduced below the critical value for wetting. However, attempts to derive more general relationships between lubricated polymer friction and wettability have not been too successful.⁵ Another way to provide rationale for reduction in friction of lubricated polymer contact is to use a plasticization argument. Rubenstein,⁶ in connection with the lubrication of nylon filaments, originally suggested that the lubricant might reduce friction by penetrating the amorphous regions of a polymer, weakening the inter-chain forces, and, thus, in turn, reducing the shear strength and the yield pressure. Assuming that the major contribution to friction arises from adhesion, the coefficient of friction is

$$\mu = \frac{\alpha\tau}{p} + \frac{(1-\alpha)\tau_l}{p}$$

where α is the proportion of load supported by polymer contact; τ and p , the shear strength and flow pressure of the polymer, respectively; and τ_l , the shear strength of the lubricant film. If both τ and p are reduced by plasticization without any change in α , then μ decreases. Alternatively, if the degree of

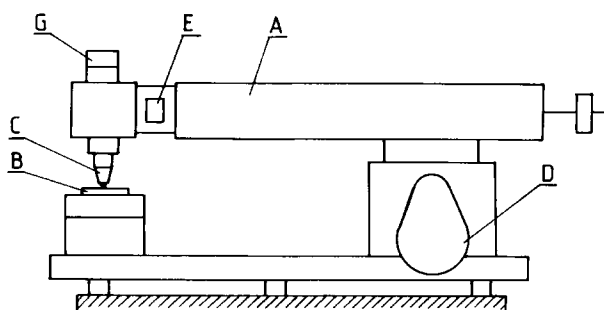


Figure 1 Slow-speed friction apparatus: (A) loading arm; (B) counterface (polymer plate); (C) slider (steel ball); (D) slow-speed electric motor; (E) friction force transducers; (G) weights.

plasticization is confined to a very thin surface layer, μ can decrease because τ decreases without any significant change in p .

This paper reports a particular type of problem that arises when a high-temperature thermoplastic polymer is lubricated with liquids containing surfactants. These additives might migrate to a significant depth into the matrix of the polymer and cause a premature form of lubrication failure under intense levels of energy dissipation. A review of lubrication failure behavior of several commercial polymers is presented and an attempt to explain the fluid-polymer interactions that can occur at the onset of lubrication failure is given.

2. EXPERIMENTAL

2.1. Test Apparatus and Procedure

(i) *Slow-speed Apparatus*

The lubrication failure process has been studied using a model contact consisting of a rigid steel ball of 6.5 mm diameter sliding over a polymer flat. The roughness of the steel ball was 0.16 μm . The apparatus is shown schematically in Figure 1. In this apparatus, a friction arm (A) was driven by a slow-speed electric motor (D). Strain gauges (E) attached to the friction arm were used to monitor the frictional force. Loading of the specimen was achieved by placing weights (G) onto the friction arm. The loading range was 5–20 N with an accuracy of ± 0.1 N. In this apparatus, a steel ball, heated in a controlled manner from an external source in the range $20\text{--}320 \pm 1^\circ\text{C}$, was slowly slid, with constant velocity of $V = 0.45 \times 10^{-3}$ m/s, over a flat polymer surface. The rate of temperature rise was typically $8^\circ\text{C}/\text{min}$.

In the case of the lubricated friction experiment,

a small and controlled amount of lubricating fluid (typically 1.0 μL) was applied to the cleaned counterface and the contact between specimen and the counterface was made. To minimize the level of lubricant oxidation at elevated temperature, the apparatus was put into a chamber through which oxygen-free nitrogen was circulated. The apparatus was placed on vibration damping washers and carefully leveled.

(ii) *Moderate-speed Apparatus*

To study lubrication failure at high-level energy dissipation brought about by frictional heating, an apparatus was devised in which the sliding conditions were such that they maximized boundary lubrication. It is very important, when studying polymer lubricated contacts, to secure boundary conditions, as only under them can the effectiveness of lubrication be fully revealed. This was achieved through application of a small quantity of lubricating fluid (typically 1.0 μL) coupled with high normal loads (up to 800 N). The apparatus is shown schematically in Figure 2. A flat surface of the polymer specimen was loaded against the steel shaft of 25.4 mm diameter. The shaft was supported horizontally by two tapered ball bearings and its surface finish was 0.16 μm . The shaft was driven by an ac motor, which, together with a variable speed gear box and pulley, was capable of continuous variation in speed over the range 120–1280 rpm. This corresponds to 0.16–1.7 m/s. Most experiments described here were carried out at the speed of 0.16 m/s. A polymer sample was mounted in the specimen holder, which, in turn, was supported by two strain gauge beams in such a way that measurement of the frictional force was possible. The load on the contact was applied continuously at the rate of 50 N/min. A typical test consisted of applying a small but carefully controlled amount of lubricating fluid to the thoroughly cleaned surface of the shaft and making contact between polymer specimen and counterface. Without external load ramp operating, the required sliding velocity was adjusted and afterward the loading device was switched on.

2.2. Material Studied

The main objective of the research described here was to determine the performance of lubricated poly(ether ether ketone) (PEEK) contacts. For comparison, poly(ether ketone) (PEK), Nylon 11, and polyacetal (PA) have also been studied.

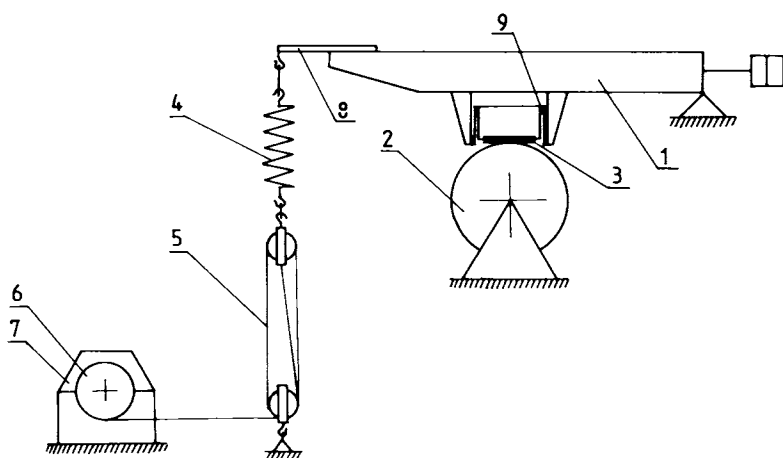


Figure 2 Moderate-speed apparatus: (1) loading arm; (2) shaft; (3) polymer specimen; (4) spring; (5) system of pulleys; (6) drum; (7) gear box; (8) beam measuring normal load; (9) beam measuring friction force.

For low-speed experiments, polymer specimens were in the form of a flat, 3 mm-thick plate. In case of moderate speed experiments, polymer specimens were produced as relatively thick films (approximately 1 mm thick) on mild steel substrates of 2 mm thickness. The adhesion of the polymer film to the substrate was enhanced by forming rather gross pores on the metal substrate into which melted polymer was pressed. The polymers investigated may be readily transformed, using thermal treatments, into a variety of morphologies. Data will be presented for samples that have been quenched from above their crystalline melting temperature, T_g , very rapidly to suppress crystallization and for samples that have been annealed for a time at a temperature below T_g , chosen for each polymer to maximize crystallinity.

A number of model lubricating fluids were used. They include dodecane, dodecane + 5% decanoic acid, and dodecane + 5% dodecylamine. The reagents were Analar grade.

2.3. Auxiliary Experiments

To study further the polymer-lubricating fluid interactions, an additional experimental technique was employed: Using a standard microhardness tester (Carl Zeiss Jena model), the static hardness of PEEK and Nylon 11 samples, subjected to various treatments, was measured. The normal loads were 25, 50, 100, and 200 g. The duration of the static test was 20 s and the apex angle of the pyramidal indenter was 136° .

3. DISCUSSION

3.1. Moderate-speed Experiments

Results obtained during moderate-speed tests follow a trend shown in Figure 3. At the beginning of the test, there is a rather rapid increase in the friction force followed by a period of relatively stable running. Eventually, a load is attained at which the friction force abruptly increases.

Figure 4 shows results obtained for dodecane as a lubricating fluid. Figures 5 and 6 show results for dodecane with 5% addition of decanoic acid and do-

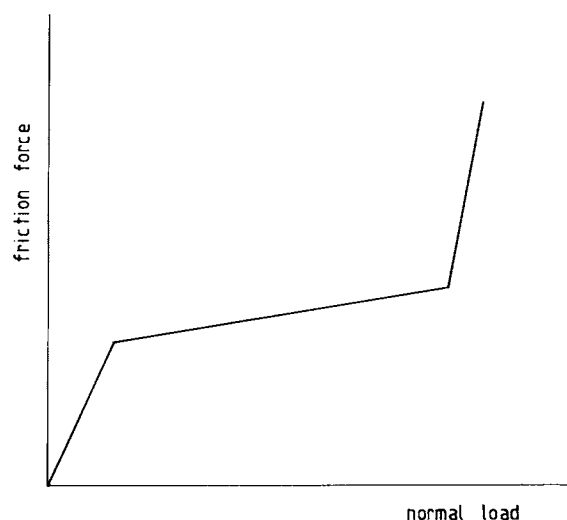


Figure 3 Characteristic features of moderate-speed test data.

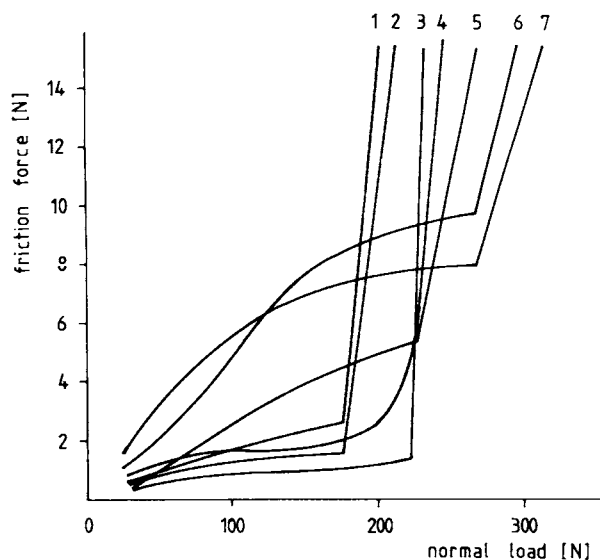


Figure 4 Moderate-speed test results: (1) PA (cooled); (2) PA (quenched); (3) Nylon 11 (cooled); (4) Nylon 11 (quenched); (5) PEK; (6) PEEK (quenched); (7) PEEK (cooled). Lubricating fluid, dodecane; sliding velocity, 0.16 m/s.

decylamine, respectively. A number of interesting features can be seen in these figures: The shapes of the curves resemble closely those of lubricated metallic contacts, although the critical loads, at which a rapid increase in friction force is observed, are much lower for polymer contacts.

No significant changes are produced by the different morphologies, although the friction is less and critical load slightly higher with the quenched sam-

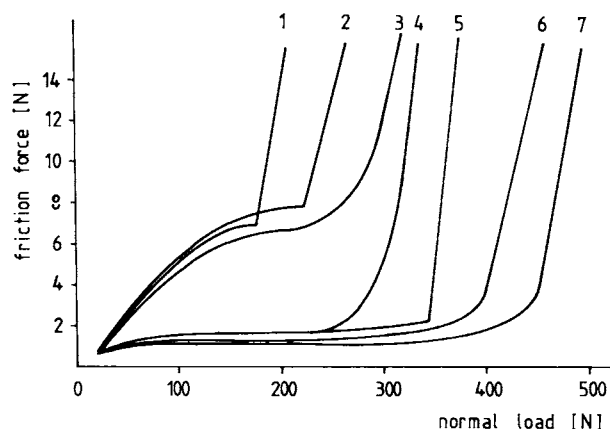


Figure 5 Moderate-speed test results: (1) PEEK (cooled); (2) PEEK (quenched); (3) PEK; (4) Nylon11 (quenched); (5) PA (quenched); (6) PA (cooled); (7) Nylon11 (cooled). Lubricating fluid, dodecane + 5% decanoic acid; sliding velocity, 0.16 m/s.

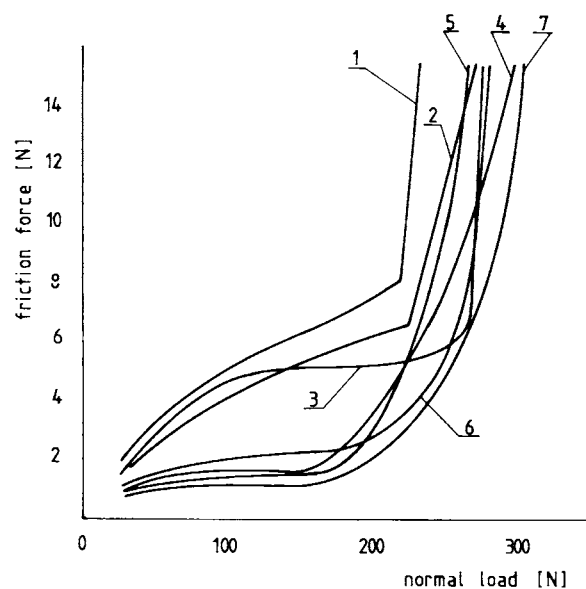


Figure 6 Moderate-speed test results: (1) PEK; (2) PEEK (cooled); (3) PEEK (quenched); (4) PA (quenched); (5) Nylon 11 (quenched); (6) PA (cooled); (7) Nylon 11 (cooled). Lubricating fluid, dodecane + 5% dodecylamine; sliding velocity, 0.16 m/s.

ples of PEEK and Nylon 11 as compared to more crystalline samples. Quite the opposite is true for PA. It is rather surprising to find that, despite a significant amount of frictional heat developed during testing, the initial morphology is preserved.

The above comments apply to the contact lubricated with dodecane, which is a pure (99.9%) hydrocarbon. A small addition of a classic boundary lubricating agent to the same *n*-alkane produces a number of differences in the behavior of polymer contacts. First of all, the performance of PEEK and PEK is not improved and the quenched material fails at higher critical load. The addition of aliphatic acid brings about an improvement in performance of Nylon 11 and PA. A strong dependence on morphology is also seen. The more crystalline the polymer, the higher the critical load.

The performance of Nylon 11 and PA was significantly improved by the addition of boundary agent to straight hydrocarbon. This response is in line with the conventional response of metallic contacts. With PEEK and PEK, however, the boundary agent produces the opposite effect.

3.2. Slow-velocity Experiments

Moderate-speed experiments are controlled, to a considerable extent, by the temperature gradient in

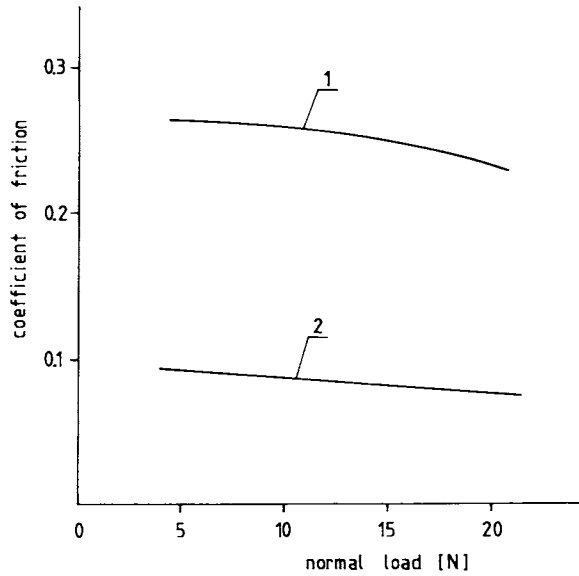


Figure 7 Slow-speed test results: (1) PEEK (cooled); (2) Nylon 11 (cooled). Dry contact; room temperature; sliding velocity, 0.45×10^{-3} m/s.

the contact zone. In an attempt to simulate the temperature gradient effect, slow velocity experiments were carried out. In essence, it was supposed that an externally heated, slowly moving counterface simulates the important features of the moderate-speed experiment.

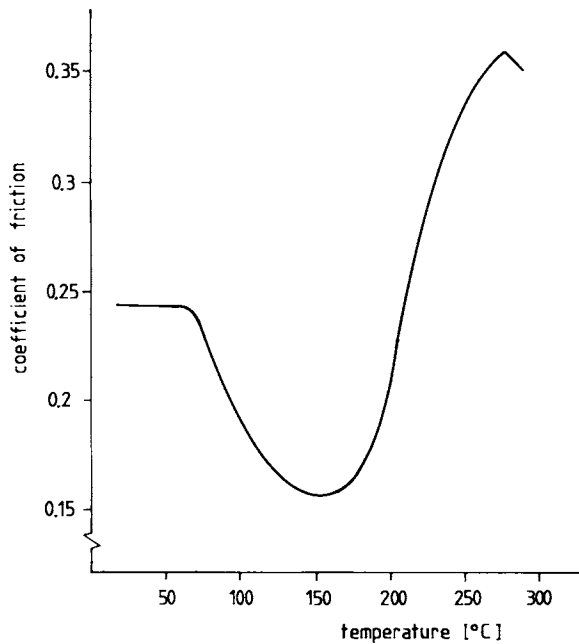


Figure 8 Slow-speed test results: polymer tested, PEEK; normal load, 10 N; dry contact.

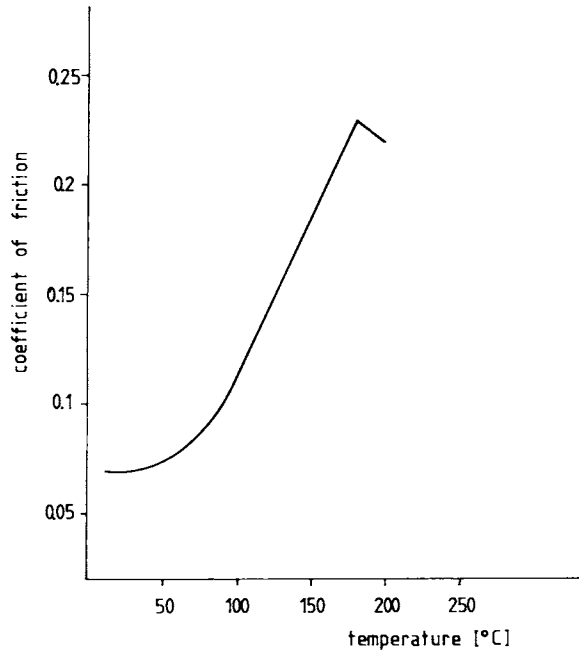


Figure 9 Slow-speed test results: polymer tested, Nylon 11; normal load, 10 N; dry contact.

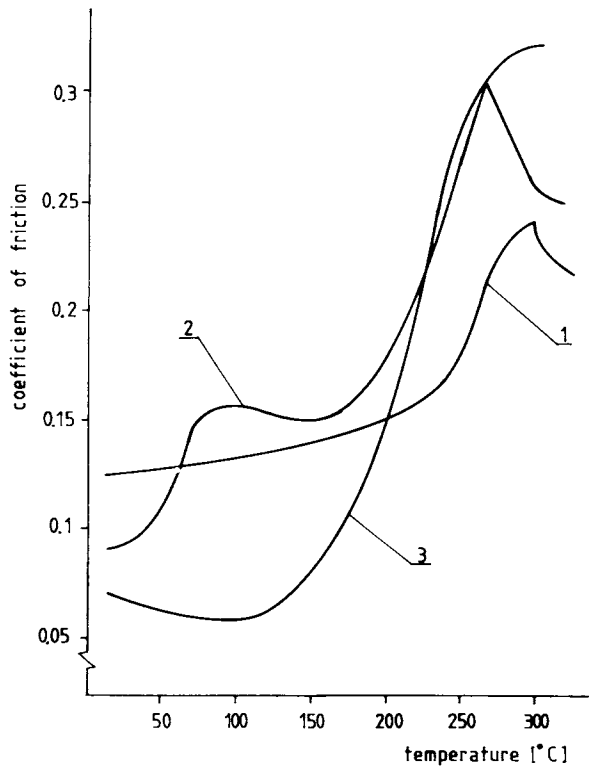


Figure 10 Slow-speed test results: polymer tested, PEEK; normal load, 10 N; (1) dodecane; (2) dodecane + 5% decanoic acid; (3) dodecane + 5% dodecylamine.

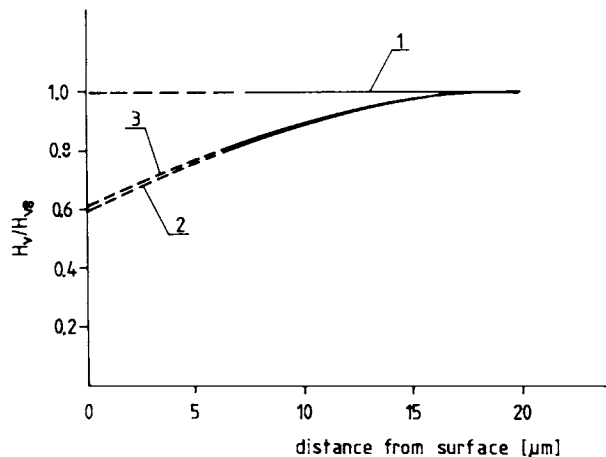


Figure 11 Microhardness test results: polymer studied, PEEK (cooled); (1) dodecane; (2) dodecane + 5% decanoic acid; (3) dodecane + 5% dodecylamine.

Because in earlier described experiments PEEK and Nylon 11 showed different behaviors, they were chosen for further studies. The difference in friction force between Nylon 11 and PEEK is shown in Figure 7. Under nominally the same conditions, the dry friction of PEEK is almost four times that of Nylon 11. The change in dry friction of PEEK with the temperature of counterface is shown in Figure 8. At room temperature, the friction is relatively high, then it decreases as the temperature increases and reaches a minimum at approximately 160°C. After that, the friction increases with temperature, at-

taining a maximum at about 280°C. The behavior of Nylon 11 in a similar experiment is depicted in Figure 9. Friction, in general, continuously increases with temperature.

Slow-velocity experiments at elevated temperatures with lubricated contacts revealed that there is no substantial difference between the dry and lubricated friction behavior of Nylon 11. However, PEEK lubricated with fluids containing acidic additives showed a considerable increase in friction at temperatures around its glass transition temperature (Fig. 10). The carboxylic acid used produces an increase in friction even at room temperature.

3.3. Auxiliary Experiments

In an attempt to explain the rather unusual response of PEEK to lubrication with fluid containing surface active additives, microhardness measurements were undertaken: Samples of PEEK and Nylon 11 were heated for 8 h at 170°C in dodecane, dodecane + 5% decanoic acid, and dodecane + 5% dodecylamine and in vacuum. Afterward, their microhardness was measured. Figure 11 shows the ratio of untreated sample microhardness, H_v , to that of treated sample, H_{v8} , as a function of the distance from the surface for PEEK, and Figure 12 shows that for Nylon 11.

Both polymers are affected by surfactants but to a different degree. It is important to note that PEEK is not affected by dodecane alone. This fact has an important significance in the mechanism leading to a premature failure of an externally lubricated

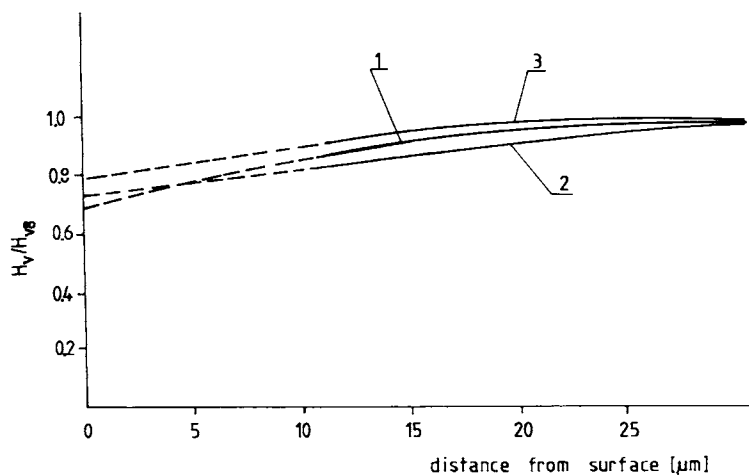


Figure 12 Microhardness test results: polymer studied, Nylon 11 (cooled); (1) dodecane; (2) dodecane + 5% decanoic acid; (3) dodecane + 5% dodecylamine.

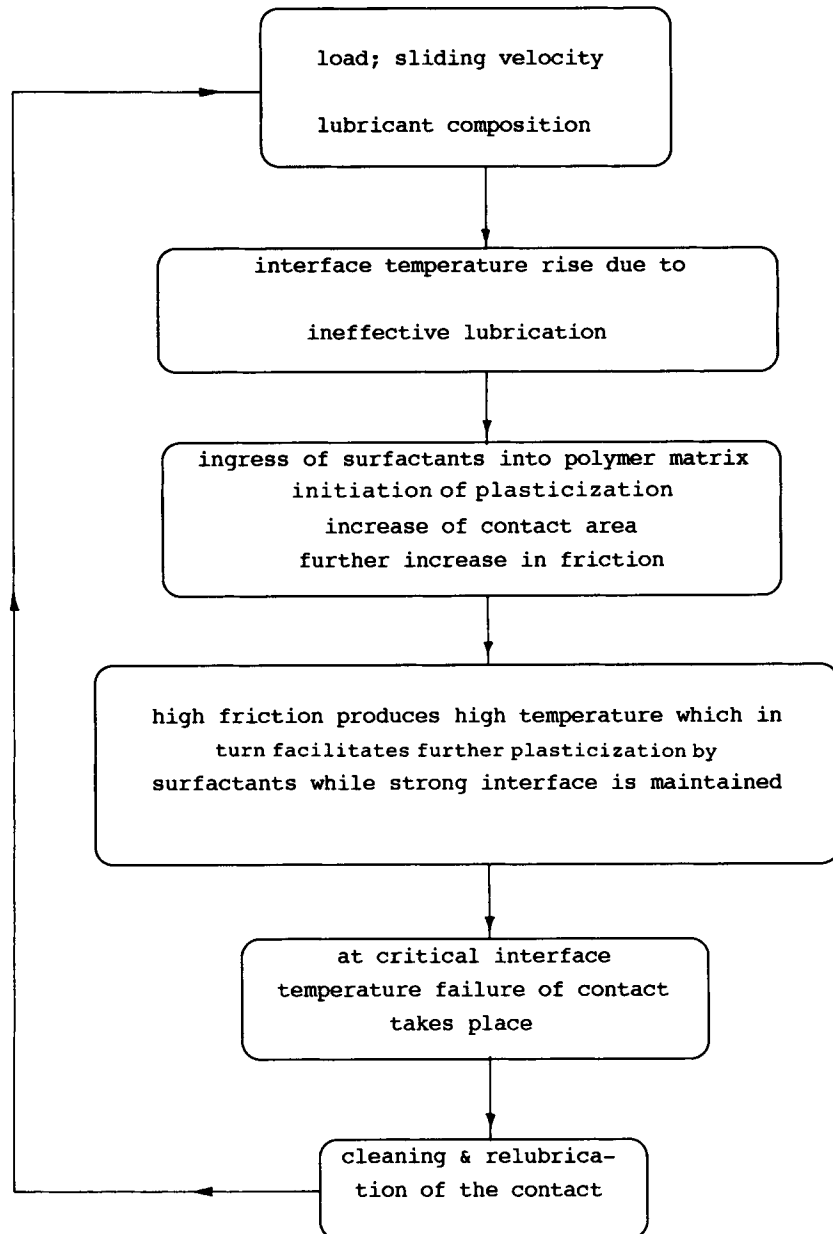


Figure 13 Stages leading to the failure of lubricated PEEK contact.

PEEK contact. The sequence of events leading to premature failure of lubricated PEEK contact is shown in Figure 13.

4. CONCLUDING REMARKS

On the basis of experimental results presented, the following explanation accounting for a premature failure of PEEK lubricated contacts may be proposed:

- (i) Premature failure of PEEK is thermally induced and promoted by the presence of certain additives in the lubricating medium.
- (ii) PEEK is not effectively lubricated by these additives and, hence, the friction is rather high.
- (iii) The additives are capable of producing slight subsurface plasticization at high interface temperatures.
- (iv) These two factors interact—High friction (due to strong interface; little change in shear strength τ) produces high temperatures, which,

in turn, create more thermal softening of the matrix and also more additive plasticization.

- (v) Softening of the subsurface (decrease in yield strength p) leads to an increase in contact area and, subsequently, to an increase in friction.
- (vi) There is some evidence that the postulated increase in the contact area is, in part, due to traction-induced junction growth,⁷ leading to the loss of surface asperity persistence.
- (vii) It is justified to say that the prevailing mode of failure of high-temperature polymers like PEEK is by phase transformation in subsurface regions.
- (viii) The behavior of lubricated PEEK contact has, in many respects, more in common with metals than with conventional thermoplastic polymers.

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