

# Scratch hardness studies of poly(ether ether ketone)

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This paper describes a study of the surface properties of poly(ether ether ketone) (PEEK) using a scratch hardness technique. A comparison of the scratch friction and the hardness values determined for amorphous and semi-crystalline PEEK shows that the crystalline polymer is harder. Studies carried out on PEEK treated with chloroform indicate that this organic solvent induces plasticization in PEEK evidenced by a change in the frictional properties and a decrease in hardness. Also, blending PEEK with other polymers, poly(ether imide) (PEI) and polytetrafluoroethylene (PTFE), demonstrates that the degree of crystallinity in PEEK is increased by the presence of such polymers. Copyright © 1996 Elsevier Science Ltd.

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## INTRODUCTION

Although normal indentation methods are more commonly used for measuring the hardness of materials, scratch hardness can also provide useful information about surface properties. The scratching technique involves drawing a rigid indenter under a known load across the surface of the specimen at a given velocity. The hardness may then be determined from the width of the resulting scratch. Qualitative estimations of the material response of a polymer may also be deduced from this technique by measurement of the scratch friction. There are certain advantages associated with scratch hardness, by comparison with indentation hardness. Scratch hardness requires comparatively simple instrumentation, as well as having the capacity to examine relatively large surface areas. Although many of the studies carried out using scratch hardness apply to metals, more recently the technique has been applied to polymers<sup>1,2</sup>.

Poly(ether ether ketone) (PEEK) is a semi-crystalline thermoplastic polymer and is currently finding use in applications in engineering because of its good mechanical properties<sup>3</sup>. One particularly important property of PEEK has been its ability to resist chemical attack; there are a very limited number of solvents for this polymer. Despite this, recent studies have shown that certain solvents can be absorbed by PEEK and cause detectable plasticization and induce crystallization<sup>4–6</sup>. One class of organic solvents which falls into this category is the chlorinated aliphatic hydrocarbons (for example, chloroform).

Polymer blends and composites have become an important subject for investigation in recent years as

they provide an economical means to the modification of polymer properties. In this study, experimental studies of two PEEK blends have been carried out. The blends include the miscible blend of PEEK and poly(ether imide) (PEI) and the dispersed system of polytetrafluoroethylene (PTFE) in PEEK. PEEK has been shown to be completely miscible with poly(ether imide) (PEI)<sup>7,8</sup> and this blend combines the good wear characteristics of PEEK with the better thermal properties of PEI. Blends involving PEEK and PTFE are useful as the friction of PEEK is significantly reduced in the blend<sup>9</sup>.

In this paper scratch hardness techniques are used to examine the changes which occur to the surface mechanical properties of PEEK in a variety of environments. The effects of the degree of sample crystallinity, the presence of a plasticising agent chloroform and blending with PEI and PTFE, are discussed.

## EXPERIMENTAL

### Materials

Polymer samples were supplied by ICI Materials, Wilton, UK. Crystalline PEEK samples were prepared by annealing the polymer at a temperature of 300°C and then allowing the samples to cool to ambient temperature. The crystallinity was estimated to be 25% by x-ray diffraction<sup>10,11</sup>. Amorphous samples were prepared by heating the samples to 400°C and immediately in cold water. The crystallinity of amorphous samples was estimated to be 0%. PEEK in the blend with PEI was prepared by blending a blend sample was prepared by blending those used to prepare the blend.

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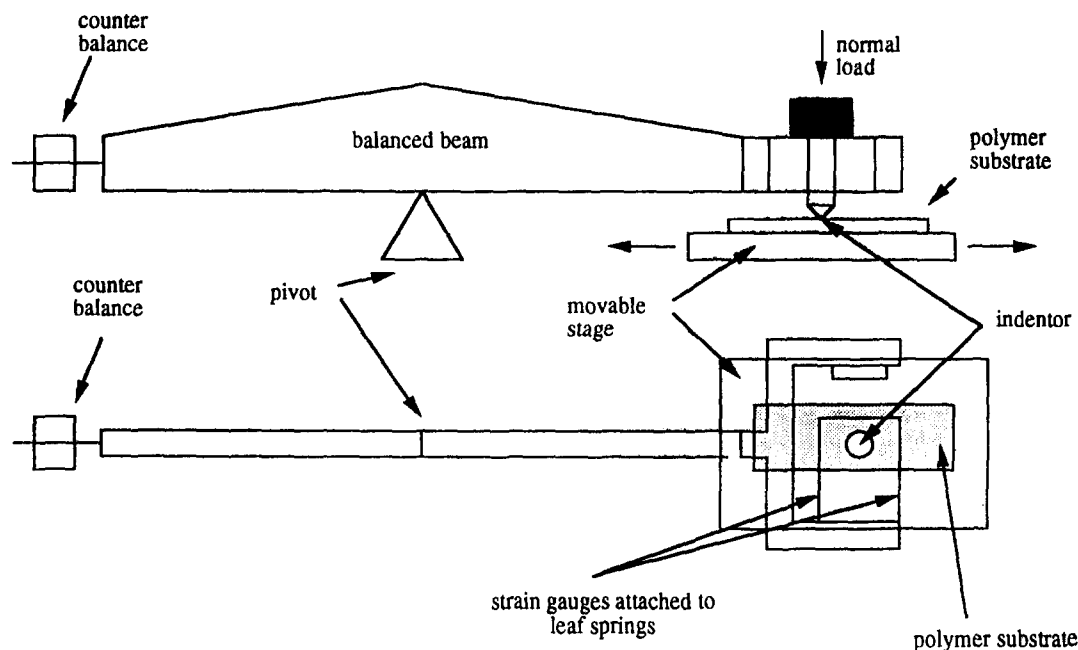


Figure 1 The scratch hardness apparatus

blend compositions used, 70 wt% PEEK/30 wt% PEI and 92 wt% PEEK/8 wt% PTFE, were chosen on the basis that these particular ratios produce the optimum changes to tribological properties<sup>7,9</sup>. The effect of chloroform on the properties of PEEK was examined by immersing crystalline PEEK in chloroform in a sealed container at room temperature for 14 days prior to the experiment.

#### Scratch hardness machine

The apparatus used for the examination of the hardness of polymers is shown schematically in Figure 1. The indenter was held on a pivoted beam so that it could be positioned orthogonally to the flat substrate. The polymer substrate was secured on the stage which was motor driven along one axis. The frictional force was measured by two strain gauges which monitored the motion of the indenter as the substrate was moved and the output was transferred to a computer. The normal load was obtained by applying known loads (in the range 10–100 g) to the indenter support unit. The effect of indenter geometry was examined by using a series of conical indentors prepared from tool steel over a range of included angles (30°, 45°, 60°, 90° and 150°). The width of the permanent scratch created by the indenter was then measured using an Olympus microscope connected to an Optomax image analyser.

#### Analysis

The frictional force produced as the indenter traversed the polymer surface was measured. The coefficient of friction,  $\mu$ , was obtained simply by dividing the frictional force by the applied normal load:

$$\mu = \frac{F}{W} \quad (1)$$

is given by:

$$\mu_p = \frac{2 \tan \theta}{\pi} \quad (2)$$

where  $\theta$  is the indenter attack angle. This expression suggests that the scratch friction coefficient due to plastic ploughing is independent of any material parameter and depends entirely on the geometry of the indenter. For the ideal case of plastic ploughing the relationship between the friction coefficient and  $\tan \theta$  is linear. Variations from this linear relationship, in the experimental values, may be used to determine the type of material response for the polymer.

It has been shown that the scratch hardness,  $H$ , may be given to a good approximation by the expression:

$$H \sim \frac{8W}{\pi d^2} \quad (3)$$

where  $W$  is the applied load and  $d$  is the scratch width<sup>1</sup>. The residual scratch width was measured after the experiment and the normal load was known. It was also possible to determine the scratch hardness as a function of the penetration depth of the indenter into the polymer surface. It was assumed, for this purpose, that there was no recovery in the depth of the residual scratch after the experiment and the penetration depth was calculated using simple geometry:

$$h = \frac{d}{2} \tan \theta \quad (4)$$

where  $h$  is the penetration depth.

## RESULTS AND DISCUSSION

### A comparison of amorphous and semi-crystalline PEEK

The coefficients of friction for amorphous and semi-crystalline PEEK as a function of  $\tan \theta$  are shown in Figure 2. Also shown in Figure 2 is the predicted friction coefficient due to plastic ploughing, calculated using equation (2). There is poor agreement between the

powden and Tabor<sup>12</sup> developed a simple model for the ploughing friction coefficient of a conical indenter for a material with a constant yield stress. This model estimates that the ploughing friction coefficient,  $\mu_p$ , is given by:

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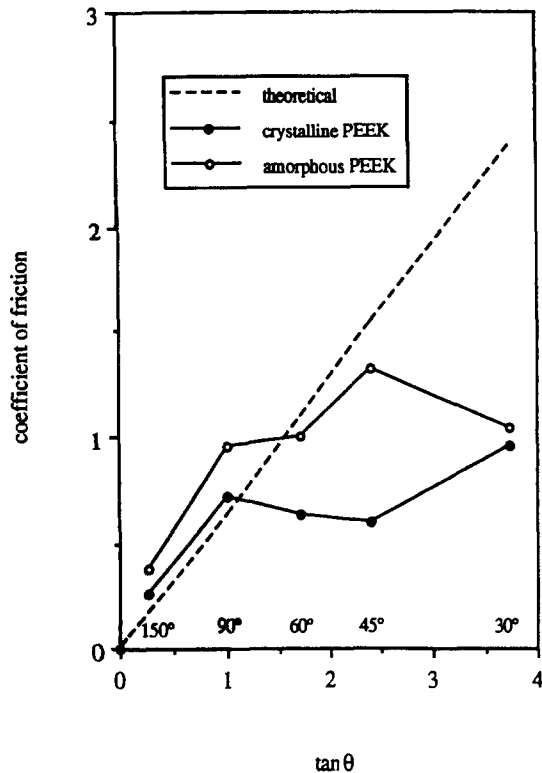


Figure 2 The effect of crystallinity on the coefficient of friction of PEEK

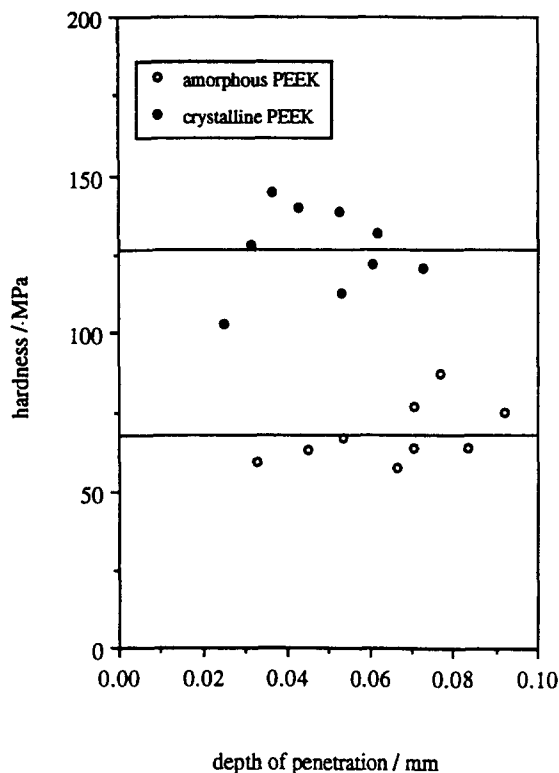


Figure 3 The effect of crystallinity on the hardness of PEEK

measured and theoretical ploughing values for most indenter angles. In the case of the 90° and 150° indentors the friction values are greater than those calculated for plastic ploughing, although for the crystalline polymer the results are relatively close to the theoretical values. This additional friction may be attributed to the work

expended in brittle cracking or fracture of the polymer. Examination of the samples by optical microscopy support this theory. The brittle fracture contribution to the friction has been observed for polymers such as PMMA<sup>1</sup>. For the other indentors ( $\leq 60^\circ$ ) the observed friction coefficients are much lower than the predicted values, and also tend to remain constant as the cone becomes sharper. Evans<sup>1</sup> observed a similar effect of the friction coefficient of PMMA with indenter angles of 30° and 45°. Evans explained the discrepancy with a machining mechanism. Chip formation occurs by shearing the material across an internal shear plane within the specimen<sup>13</sup>. The shear plane angle is less than the attack angle of the indenter and is independent of the indenter used. Plastic flow then occurs at an angle less than the cone attack angle. The ploughing friction force is thus governed by the shear plane angle, rather than the attack angle of the cone. Figure 2 also shows that the values of the friction coefficients of the two samples of PEEK are dependent on the crystallinity of the polymer. For each cone angle, the friction coefficient for amorphous PEEK is higher than those values determined for crystalline PEEK and closer to the theoretical plastic values. This may indicate the amorphous polymer responds in a manner more closely related to that of a purely plastic material.

The scratch hardness of both amorphous and crystalline PEEK was calculated from the resulting scratch widths. Figure 3 shows the hardness of amorphous and semi-crystalline PEEK as a function of the depth of penetration of the indenter during sliding. The scatter among these results is relatively high, but when a linear fit is applied, a clear difference in the magnitude of the hardness is observed for the amorphous and crystalline polymers. The hardness of crystalline PEEK is notably higher than that of the amorphous material. The hardness in both cases appears to remain relatively constant until depths of at least 100  $\mu\text{m}$ .

#### The effect of chloroform on PEEK

Figure 4 illustrates the effect of chloroform on the coefficient of friction of PEEK. For indenter angles of 90° and 150° the friction values for PEEK treated with chloroform are slightly higher than those values observed for the untreated original PEEK sample. This indicates that there is a slight increase in the amount of brittle fracture occurring with these angles. The friction observed for the chloroform treated sample at 60° is significantly increased. The value is greater than that predicted for plastic ploughing and also indicates a significant contribution to the friction due to brittle fracture. The friction coefficients observed when 30° and 45° indentors are applied to chloroform-treated PEEK are greater than those observed for the original crystalline samples. These increases indicate that there is a greater plastic ploughing contribution to the friction after PEEK is exposed to chloroform and the values approach those calculated for plastic ploughing.

The effect of chloroform on the scratch hardness of PEEK has also been examined and is illustrated by Figure 5. The hardness values for untreated crystalline PEEK are shown, along with those determined for crystalline PEEK after exposure to chloroform. A linear fit indicates that the values calculated for the chloroform-treated samples are lower than those of the

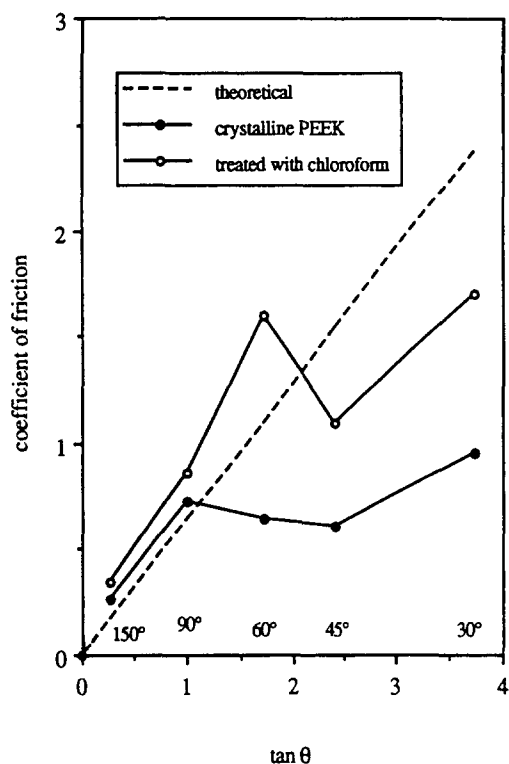


Figure 4 The effect of chloroform on the coefficient of friction of PEEK

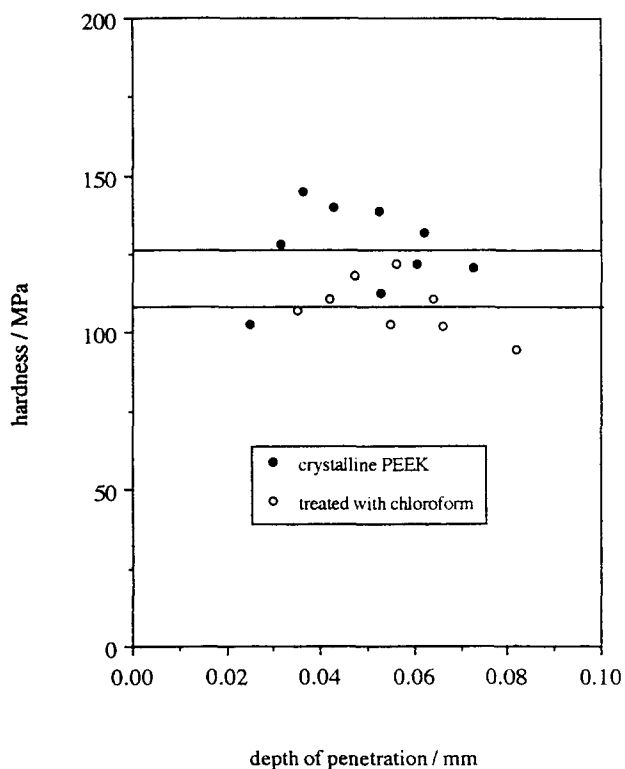


Figure 5 The effect of chloroform on the hardness of PEEK

original crystalline sample. This reduction may be explained by a softening of the PEEK surface due to the presence of chloroform. Chloroform acts as a plasticizer and the softening of PEEK allows the indenter to penetrate the polymer to a greater depth. This, in turn, produces a greater scratch width and hence

decreases the hardness. There is no convergence of the hardness values for the untreated and treated samples and this observation indicates that the plasticization of PEEK by chloroform occurs at depths greater than 100  $\mu\text{m}$ , depths which are beyond the scope of the hardness experiments carried out here.

#### Blending PEEK with PEI

The scratch friction of semi-crystalline crystalline PEEK, PEI and a blend of these two polymers has been examined and compared. Figure 6 illustrates the friction coefficients of each and their dependence on the indenter geometry. The friction of crystalline PEEK shown in this figure was discussed earlier. The coefficient of friction of PEI as a function of indenter geometry behaves in a very different manner to that of PEEK. The scratch friction mechanism for PEI appears to be that of plastic ploughing as the friction coefficients correspond more closely to the theoretical values calculated using equation (2) (also shown in Figure 6). Examination of the friction coefficients determined for a 70 wt% PEEK/30 wt% PEI blend shows that the values are similar to the frictional properties of crystalline PEEK. There are some minor differences in friction values, such as for the 30° indenter, but it is difficult to make any clear conclusions regarding changes to the material response of the polymer based on such observations.

Figure 7 compares the hardness of PEEK, PEI and a 70 wt% PEEK/30 wt% PEI blend as a function of indenter penetration depth. The hardness values of 100 wt% PEI are considerably lower than those observed for crystalline PEEK. A blend of these two polymers produces hardness values significantly higher than those observed for the unblended crystalline PEEK. It is postulated that the reason for the observed increase in hardness is that there is

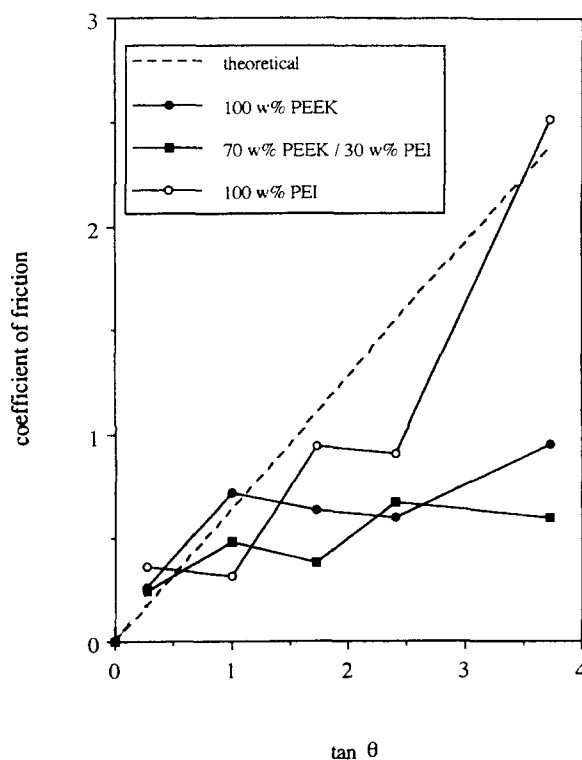


Figure 6 The effect of PEI on the coefficient of friction of PEEK

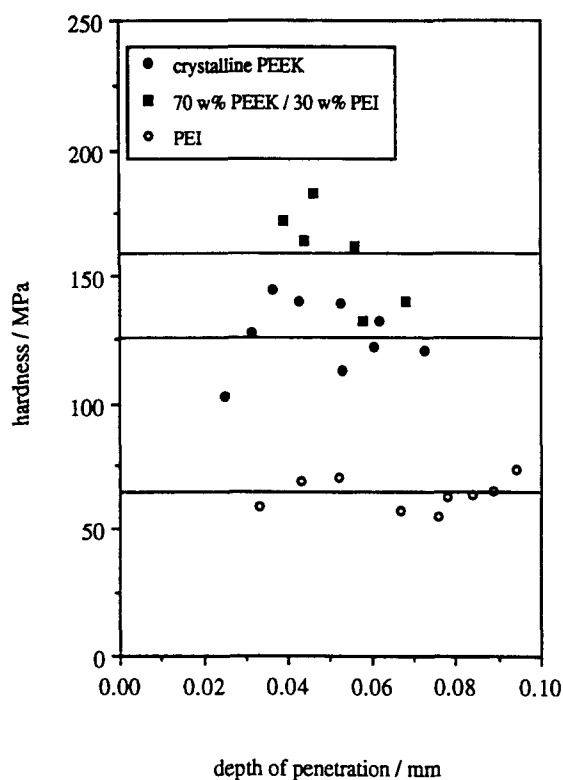


Figure 7 The effect of PEI on the hardness of PEEK

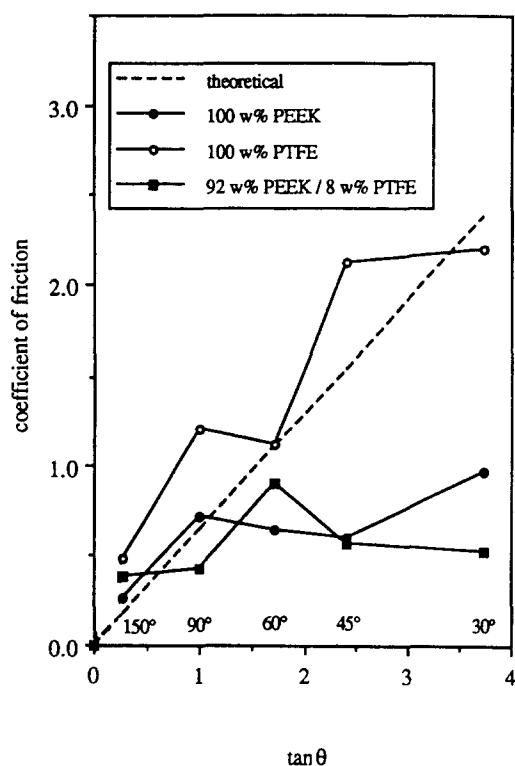


Figure 8 The effect of PTFE on the coefficient of friction of PEEK

a higher percentage of crystalline PEEK in the blend compared to the unblended PEEK samples. It has already been shown in that crystalline PEEK shows higher hardness values than those observed for the amorphous polymer. This idea is supported by Raman spectroscopic data<sup>11</sup> which demonstrated that the amount of crystallinity induced in PEEK is increased by blending with PEI.

#### Blending PEEK with PTFE

The friction coefficients of PTFE and a 92 wt% PEEK/8 wt% PTFE blend have also been determined as a function of  $\tan \theta$  and are shown in Figure 8. The coefficients of friction for crystalline PEEK and theoretically calculated plastic ploughing values discussed previously are also shown in Figure 8. The scratch friction of PTFE was reported by Evans<sup>1</sup> and his study showed that the frictional response of PTFE follows the theoretical plastic ploughing model. There are some differences observed between the PEEK friction and that of the PEEK/PTFE blend, but these are not significant enough to indicate major changes to the material response of the polymer.

Figure 9 shows the hardness values determined as a function of the indenter penetration depth for PTFE, a 92 wt% PEEK/8 wt% PTFE blend and crystalline PEEK. The hardness values observed for PTFE are, not unexpectedly, much lower than those observed for crystalline PEEK. It has already been shown by the friction results that PTFE is a more ductile material. This property allows the indenter to penetrate the surface of PTFE more easily than in the case of a polymer such as PEEK. The resulting scratch width is therefore greater and so the hardness value is less.

The hardness values determined for the PEEK/PTFE blend in an altogether different manner to those of the unblended component homopolymers. While the hardness of the constituent polymers is independent of the penetration of the indenter, the hardness of the blend increases dramatically over a narrow range of depth. This trend indicates that the blend is softer close to the surface, where hardness values are similar to those observed for unblended PTFE, and then become harder with hardness increasing to values greater than those

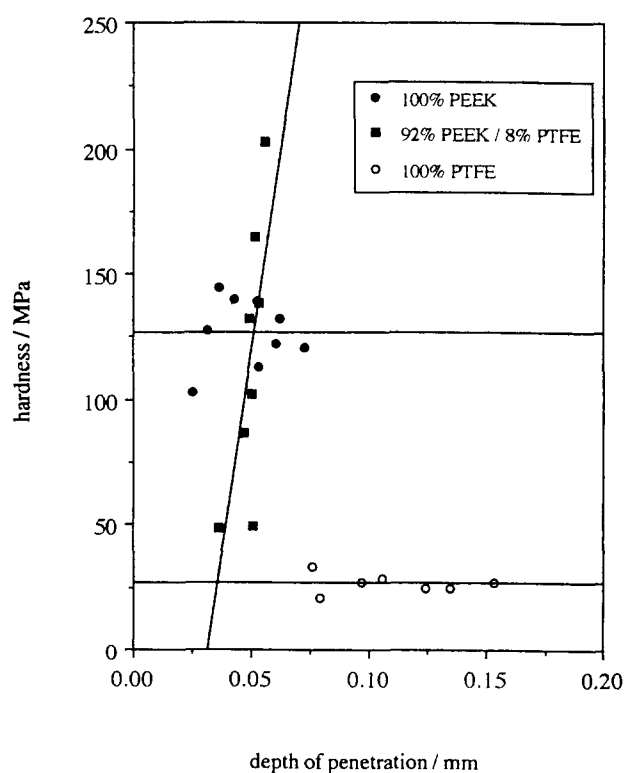


Figure 9 The effect of PTFE on the hardness of PEEK

observed for unblended crystalline PEEK. A possible explanation for these observations is that there is phase segregation of the constituent homopolymers near the surface of the blend. PTFE appears to migrate to the surface of the blend and hence the low hardness values observed at the surface. This leaves a higher concentration of crystalline PEEK in the underlying regions where the hardness is observed to be considerable. The transition between the two phases occurs over a relatively narrow range (30–50  $\mu\text{m}$ ). It is also interesting to note that the magnitude of the hardness values observed for the blend at the highest load is greater than that observed for the unblended crystalline PEEK. This indicates that the PEEK at these depths may be more crystalline than that in the unblended polymer, as greater hardness values indicate a higher percentage of crystalline material. It appears that the presence of PTFE induces more crystallinity in PEEK when these polymers are mixed in this immiscible blend. This observation is consistent with spectroscopic data<sup>14</sup> which also showed an increase in PEEK crystallinity in the presence of PTFE.

## CONCLUSIONS

A comparison of the frictional behaviour and the hardness of amorphous and crystalline PEEK was carried out. Several friction mechanisms were observed for both forms of PEEK. When sharper indentors were applied a machining mechanism was observed, while for blunter indentors a brittle fracture contribution to the friction was observed. However, amorphous PEEK showed friction coefficients of magnitudes closer to those calculated for a theoretical plastic ploughing mechanism. An examination of the hardness values of both amorphous and crystalline PEEK showed that the hardness of crystalline PEEK is notably higher than that of amorphous PEEK. Both forms of PEEK have hardness values which are independent of the depth of penetration of the indenter.

The effect of chloroform on the material properties of crystalline PEEK was studied. Significant changes to the frictional behaviour of PEEK were observed due to the presence of chloroform. When sharper indentors were applied to the chloroform-treated surface the friction coefficients produced approached those predicted for a plastic ploughing mechanism. Also, the hardness of PEEK was shown to be reduced after treatment with chloroform. It was concluded from these results that chloroform causes plasticization of PEEK.

A study of the effect of blending PEEK with the polymer PEI on the scratch friction and hardness was also carried out. PEI is a more ductile material than PEEK and an examination of the coefficient of friction during scratching indicated that PEI shows mainly plastic ploughing behaviour. However, blending PEI with PEEK did not show any significant changes in the frictional behaviour of PEEK. But differences were certainly observed in the hardness values. PEI shows a hardness considerably lower than that of PEEK.

Blending of these polymers produced hardness values higher than those observed for the unblended crystalline PEEK. It was proposed that the amount of crystallinity in PEEK is, in fact, increased by the presence of PEI, a theory supported by spectroscopic data.

The effect of blending another polymer, PTFE, with PEEK on the properties of the latter has also been investigated. Like PEI, PTFE is a more ductile material than PEEK. However, no significant changes were observed in the scratch frictional properties of PEEK due to the presence of PTFE. Significant changes were noted, however, to the hardness values of PEEK after blending with PTFE. The results of this study showed that phase segregation of the constituent polymers in this blend occur. PTFE migrates to the surface while PEEK occupies the underlying regions. The data also showed that the PEEK in this blend is more crystalline than unblended crystalline PEEK produced under the same conditions. The conclusions made here regarding the PEEK/PTFE blend are supported by data presented in the spectroscopic studies.

Thus, it has been shown in this study that scratch hardness provides an effective technique for the examination of the surface properties of polymers. The scratch friction has been shown to be sensitive to the nature of the energy dissipation processes. This information, coupled with the sensitivity of the hardness values, allows conclusions to be deduced about the material properties of polymers.

## ACKNOWLEDGMENT

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