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The effect of crystallinity on the scratch hardness of poly(ether ether ketone)

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Summary

This paper describes a study of the surface properties of the poly(ether ether ketone) (PEEK) using a scratch hardness technique. A comparison of the hardness values determined for amorphous and crystalline PEEK shows that the crystalline polymer is harder. In addition, comparion of the scratch frictional behaviour indicates several friction mechanisms apply for this polymer.

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 indentor 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 (1,2).

Poly(ether ether ketone) (PEEK) is a semi-crystalline thermoplastic polymer. PEEK is currently finding use in high performance composites and applications in aerospace and automative engineering because of its good mechanical properties (3). The degree of crystallinity in PEEK has important consequences for the applicability of this polymer in engineering. A number of experimental approaches have been employed in previous studies to investigate the morphology of PEEK, including X-ray crystallography (4-6), differential scanning calorimetry (DSC) (5), Raman spectroscopy (7,8) and infrared spectroscopy (9). In this study, scratch hardness techniques are used to examine the surface mechanical properties of PEEK as a function of crystallinity. The scratch hardness and friction of crystalline and amorphous PEEK are compared.

Experimental

Materials

PEEK samples were supplied by ICI Materials, Wilton, U.K. Crystalline PEEK samples were produced by annealing the polymer at a temperature 400-420°C and then allowing the samples to cool gradually to ambient temperature. The crystallinity of the samples were estimated to be 25% using DSC. Amorphous samples were produced by heating the samples to 400-420°C and then quenching immediately in cold water. The crystallinity of the amorphous samples was estimated to be negligible.

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Scratch hardness machine

The apparatus used for the examination of the hardness of PEEK is shown schematically in Figure 1. The indentor 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 indentor as the substrate was moved, and the output was transferred to a computer. The normal load was obtained by applying known loads to the indentor support unit. The effect of indentor geometry was examined by using a series of conical indentors prepared from drill steel over a range of included angles (30°, 45°, 60°, 90° and 150°). The width of the permanent scratch created by the indentor was then measured using an Olympus microscope connected to an Optomax image analyser.

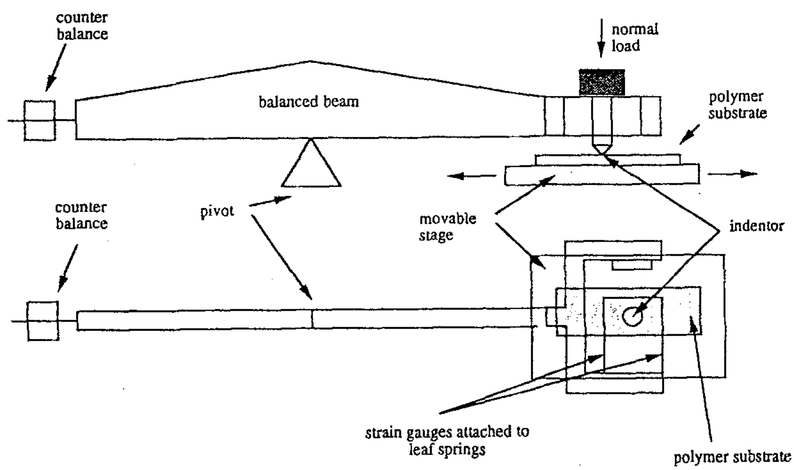

Figure 1. Scratch hardness apparatus.

Analysis

The frictional force produced as the indentor traversed the polymer surface was measured. The coefficient of friction (μ) was obtained simply by dividing the frictional force (F) by the applied normal load (W):

$$\mu = \frac{F}{W} \tag{1}$$

Bowden and Tabor (10) developed a simple model for the ploughing friction coefficient of a conical indentor for a rigid plastic material with a constant yield stress. This model indicates that the ploughing friction coefficient (μ_p) is given by:

$$\mu_p = \frac{2 \tan \theta'}{\pi} \tag{2}$$

where θ is the indentor 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 indentor. For the ideal case of plastic ploughing the relationship between the friction coefficient and tan θ is linear. Variations in the experimental values from this linear relationship 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:

$$H \sim \frac{8W}{\pi d^2} \tag{3}$$

where d is the scratch width (1). The residual scratch width was measured after each experiment and it was possible to determine the scratch hardness as a function of the penetration depth of the indentor into the polymer surface. It was assumed, for this study, that there was no recovery in the depth of the residual scratch after the experiment and the penetration depth was calculated using simple geometry:

$$h = \frac{d}{2} \tan \theta' \tag{4}$$

where h is the penetration depth.

Results and discussion

The coefficients of friction for amorphous and crystalline PEEK as a function of tan θ′ 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 no close agreement between the measured and theoretical ploughing values for most indentor 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 is attributed to the work expended in brittle cracking or fracture of the polymer. The brittle fracture contribution to the friction has been observed for polymers such as poly(methyl methacrylate) (PMMA) (1). For the other indentors (≤60°) the observed friction coefficients are much lower than the predicted values, and also tend to remain constant as the cone become sharper. Evans (1) observed a similar effect for the friction coefficient of PMMA with indentor angles of 30 and 45°. Evans explained the discrepancy with a machining mechanism, resulting in chip formation. Chip formation occurs by shearing the material across an internal shear plane within the specimen (11). The shear plane angle is less than the attack angle of the indentor and is independent of the indentor 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. Where the friction coefficient is independent of the cone angle, the actual value is higher in the case of amorphous PEEK. This may indicate the amorphous polymer responds in a manner more closely related to that of a purely plastic material.

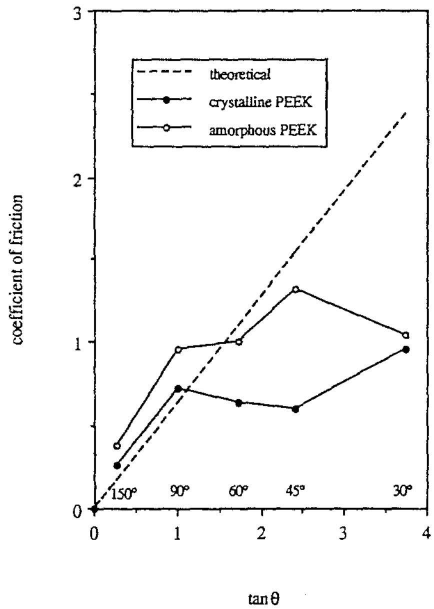

Figure 2. The effect of crystallinity on the coefficient of friction of PEEK.

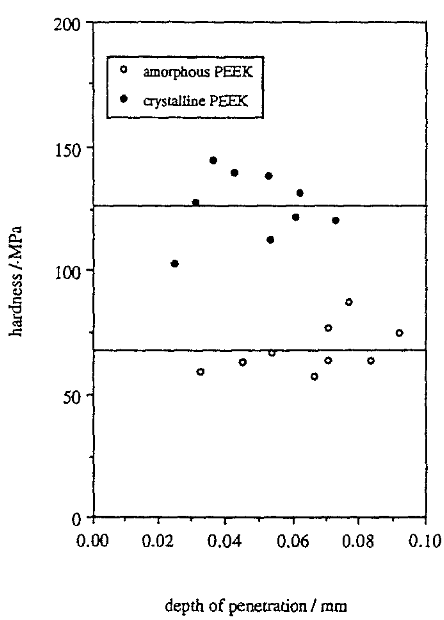

Figure 3. The effect of crystallinity on the scratch hardness of PEEK.

The scratch hardness values of both amorphous and crystalline PEEK were calculated from the resulting scratch widths. Figure 3 shows the hardness of amorphous and crystalline PEEK as a function of the depth of penetration of the indentor during sliding. 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 μm.

Conclusions

A comparison of the scratch 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 shows 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 indentor.

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