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Evaluation of Young's modulus of polymers from Knoop microindentation tests

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The Young's modulus to hardness ratio of small-scale polymer specimens is measured by means of a Knoop indentation procedure. The technique assumes that the extent of elastic recovery of a Knoop indent is linearly related to the modulus to hardness ratio. A semiempirical linear relationship is proposed for the elastic recovery of the small diagonal of a Knoop indenter as a function of the modulus to hardness ratio for polymer materials, provided that indenting loads of at least 4 N are used. The major benefit of the procedure is that measurements of Knoop microhardness and indentation recovery enable the evaluation of Young's modulus of small-scale polymer specimens. © 1998 Elsevier Science Ltd. All rights reserved.

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Introduction

It is sometimes necessary to know the Young's modulus of small- scale polymeric areas (spherulites, transcrystalline layers, local phases in blends), or of small specimens, for which the use of common mechanical methods (such as tensile testing) is impractical. A convenient but indirect technique is the Vickers microindentation method by which a small, symmetrical, pyramidal diamond tip probes the material's surface resistance to penetration. Young's modulus may then be obtained, since appropriate theoretical relationships between the Vickers hardness (H_v) and the modulus (E) are generally available[1–3]. For example, Lawn and Howes[1] developed a technique for measuring H_v and E based on the assumption that the extent of elastic recovery in the depth of a Vickers indent is linearly related to the ratio H_v/E. If the hardness of anisotropic specimens is needed, an elongated Knoop tip may be used, as the Vickers indenter is not orientation-sensitive and is thus not very effective for measuring direction-dependent properties of anisotropic materials. However, in this case, the theoretical link between Knoop hardness (H_k) and Young's modulus is far from being well established. Marshall *et al.*[4] developed a simple semiempirical method to determine the H_k/E ratio (and thus the link between E and H_k), but only brittle (ceramic) materials were studied. The method is based on the measurement of the elastic recovery of a Knoop indentation. Thus, if upon indentation loading the lengths of the long and short diagonals of the pyramidal imprint are a and b, respectively, upon unloading the diagonal lengths decrease to a_{rec} and b_{rec} due to partial recovery of the indented material. The Knoop indenter geometry requires that $a/b = 7.11$, but this may not be true after unloading. Indeed, Marshall *et al.*[4] found that elastic recovery of ceramic materials reduces the length b of the shorter diagonal more than the length a of the longer diagonal. In fact, the key observation of these authors is that there is a functional relationship between the extent of recovery of a material, b_{rec}/a_{rec}, and the ratio H_k/E. Thus, materials for which recovery is negligible ('rigid/plastic' materials, $a = a_{rec}$, $b = b_{rec}$) have a relatively low H_k/E ratio, whereas those for which recovery is very large ('highly elastic' materials, $a \gg a_{rec}$, $b \gg b_{rec}$) have a relatively high H_k/E ratio. Assuming that recovery of the longer diagonal is negligible ($a_{rec} \approx a$), which is supported experimentally, Marshall *et al.*[4] derived a simple linear form for the functional dependence between b_{rec}/a_{rec} and H_k/E, as follows:

$$\frac{b_{rec}}{a_{rec}} \approx \frac{b_{rec}}{a} = \frac{b}{a} - \alpha\frac{H_k}{E} \tag{1}$$

where the slope α is a numerical constant which will be discussed later. For ceramics, it was indeed demonstrated experimentally[4] that the extent of recovery is linearly dependent on the H_k/E ratio and that b_{rec}/a_{rec} is independent of the indenter load in the 10–100 N range. (In fact, load independence was demonstrated for an even wider range, 2–700 N, in the case of Si_3N_4.)

The objective of the present work was to study the validity of equation (1) for polymer materials, so that measurements of Knoop microhardness and indentation recovery could lead to the evaluation of Young's modulus of small-scale polymeric specimens, or of small local polymer areas with distinctive microstructures. No attempt was made in this work to correlate our microindentation measurements with microstructural details[5], as we are primarily concerned with mechanical effects.

Experimental

Microindentation and tensile tests were performed using five types of commercially available polymers, namely poly(vinyl chloride) (PVC), polycarbonate (PC), isotactic polypropylene (iPP), poly(methyl methacrylate) (PMMA) and polyoxymethylene (POM). Five dogbone-like specimens were prepared according to ASTM D-638M specifications for each of the polymer types. The specimens were first microindented and then tested in tension.

Microindentations were performed using a Leitz microhardness tester attached to an optical microscope (Leitz

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Metallux 3) equipped with a video imaging system (Aplitec MSV-800).

Indentations were produced using a Knoop indenter. Loads of 0.05, 0.1, 0.25, 2 and 4 N were applied, using a 10 s loading cycle. The lengths of both imprinted diagonals were measured within 30 s following indentation, using a Leitz hardness-measuring digital eyepiece, equipped with a Leitz computer counter printer (RZD-DO). The microhardness (H_k) values were calculated using the formula

$$H_k = 14.23 \frac{P}{d^2} 10^{-6}$$

where H_k is expressed in megapascals, the applied force P is in newtons, and the diagonal d is in metres. Fifteen imprints were made on each polymer type, under each load, using three of the five specimens in each case. The imprint sites were located in the end areas of the dogbone specimens (*i.e.* the areas that were to be clamped in the tensile testing apparatus).

Tensile tests were then performed with an Instron 4502 apparatus. Five tests were performed for each polymer type, at a cross-head speed of 1 mm min^{-1}. Specimen deformation was measured by extensometry.

Results and discussion

The test results of all microhardness (H_k) and Young's modulus (E) measurements are presented in *Table 1*. As can be seen, H_k decreases as the indenter load increases, in all cases. This may be explained by the fact that when the load increases, the indented area also increases and more defects are activated, leading to a decrease in hardness. The variability in hardness measurements is also much larger at lower indenting loads, and there is a sense that the data at higher indenting loads are more reliable. Taking PVC as a typical example, this is confirmed by the data shown in *Figure 1*, where both the Knoop impression dimensions, b_{rec}/a_{rec}, and the hardness to modulus ratio, H_k/E, were plotted as a function of the applied indenting load. As can clearly be seen, the behaviour of both ratios is significantly different at low and high loading levels. The important finding is that at higher load levels, both b_{rec}/a_{rec} and H_k/E become progressively independent of the load. Based on these observations, we have plotted in *Figure 2* the variations of the Knoop impression dimensions, b_{rec}/a_{rec}, with hardness to modulus ratio, H_k/E, obtained with indenting loads of 2 and 4 N. For comparison, a low load data set ($P = 0.05$ N) is also shown. Clearly, the data at higher loads are much less scattered (the scatter of the data obtained at 0.1 and 0.25 N, not shown on the graph for clarity, is also large). The regression line parameters for the polymer data are shown in *Table 2*, from which two interesting points emerge for indentations performed at progressively higher loads: (1) the ratio b/a converges towards the necessary value ($1/7.11 = 0.14$) imposed by the Knoop indenter geometry; (2) the slope α converges towards a value that is close to the value of α found by Marshall *et al.*[4] for ceramics ($\alpha = 0.45$). Marshall *et al.*[4]

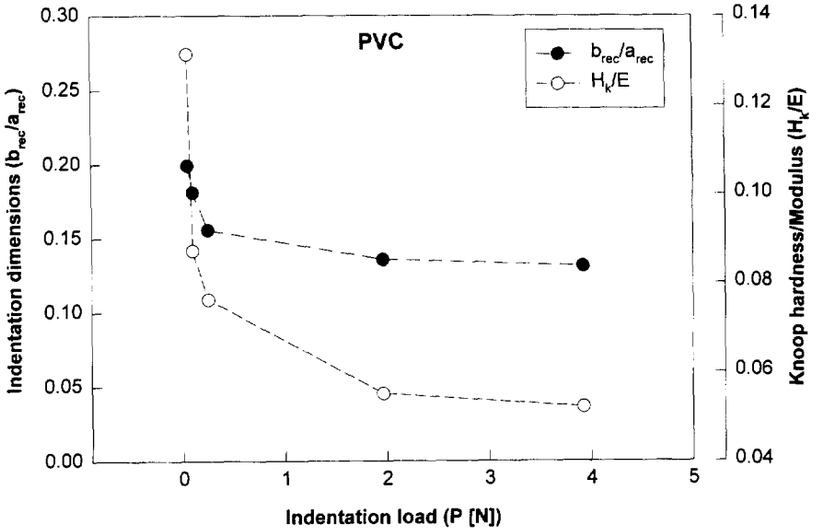

Figure 1 Knoop impression dimension ratio b_{rec}/a_{rec}, at 30 s recovery, and microhardness to modulus ratio, H_k/E, as a function of indenting load P, for PVC

Table 1 Knoop microhardness (H_k)[a] and Young's modulus (E) of the polymer materials tested

Material	H_k (MPa)					E
	($P = 0.05$ N)	($P = 0.1$ N)	($P = 0.25$ N)	($P = 2$ N)	($P = 4$ N)	(GPa)
PVC	347 ± 85	231 ± 20	202 ± 20	146 ± 5	138 ± 5	2.64 ± 0.1
PC	477 ± 180	307 ± 80	250 ± 65	242 ± 5	223 ± 5	3.22 ± 0.12
iPP	336 ± 60	268 ± 50	218 ± 25	192 ± 5	179 ± 5	3.10 ± 0.14
PMMA	278 ± 25	206 ± 10	181 ± 10	241 ± 10	222 ± 5	2.34 ± 0.0.15
POM	482 ± 280	341 ± 210	301 ± 140	225 ± 10	213 ± 1	2.94 ± 0.25

[a]The microhardness data were obtained at five different levels of load P

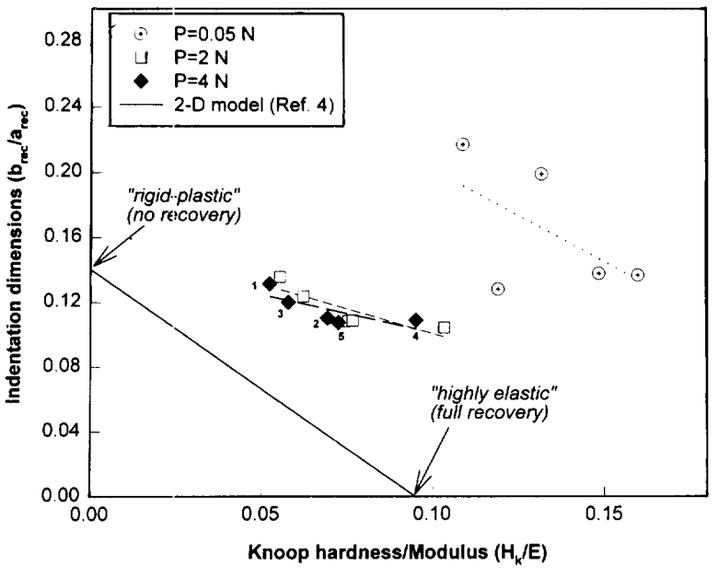

Figure 2 Variation of Knoop impression dimensions, b_{rec}/a_{rec}, with microhardness to modulus ratio, H_k/E, under 0.05, 2 and 4 N indenting loads, for five polymers: (1) PVC; (2) PC; (3) iPP; (4) PMMA; (5) POM

Table 2 Regression parameters for Marshall's linear model (equation (1)) for polymers, at different indenting loads

Load (N)	b/a	α
0.05	0.41	1.74
0.1	0.33	1.85
0.25	0.25	1.40
2	0.16	0.61
4	0.15	0.47

proposed an approximate theoretical model for the linear parametric dependence between b_{rec}/a_{rec} and H_k/E. This was based on a calculation of the elastic recovery of a simplified two-dimensional elliptical indentation, with major and minor axes in the same ratio as the Knoop indentation diagonals. They derived a linear relationship that has the form of equation (1) with parameters $b/a = 0.143$ (imposed by the Knoop geometry) and $\alpha = 3/2$ (imposed by a two-dimensional elliptical hole geometry). This theoretical line is plotted in *Figure 2*. It is interesting to note that the ceramic data of Marshall *et al.*[4] (obtained under high indenting load) and the polymer data presented here (also under high indenting loads) are in close proximity to each other (although the H_k/E ranges are slightly different, from about 0.01 to 0.075 for ceramics, and from about 0.05 to 0.1 for polymers). They are also equally away from the theoretical line sketched in *Figure 1*. Moreover, as already mentioned, the experimental slope α for both groups of materials, ceramics and polymers, is nearly equal (about 0.45 under high loads) and is much lower than that of the elliptical hole model (1.5), which is probably due to the smaller extent of recovery in the more constrained three-dimensional indentation, as suggested by Marshall *et al.*[4]. The value of the intercept b/a for polymers is about 0.15 under high loads, close to the value (0.143) imposed by the geometry of the Knoop indenter (for ceramics, Marshall *et al.*[4] imposed the necessary intercept but the experimental intercept was close to the theoretical one anyway, (see *Fig. 2* in Ref. [4]). From the above considerations and results, we conclude that the semiempirical method proposed by Marshall for ceramics is applicable to polymers as well, provided that relatively high indenting loads are used (the same restriction applied for ceramics, but with higher loads, in the range 10–100 N).

Figure 2 may be used to determine Young's modulus of small polymer specimens, even possibly small anisotropic polymer areas such as transcrystalline interlayers. A typical procedure would require the carrying out of a Knoop indentation test under a load of at least 4 N, extracting the hardness H_k and the 30 s b_{rec}/a_{rec} indentation ratio, then assessing the modulus from the corresponding abscissa value. With indenting loads of at least 4 N, the following correlation between the Knoop impression dimensions (within 30 s of load release) and hardness to modulus ratio was found to be valid for polymers:

$$\frac{b_{rec}}{a} = 0.148 - 0.473\frac{H_k}{E} \qquad (2)$$

Some inherent limitations exist which are difficult to quantify at this point. For example, the sensitivity of polymers to time-dependent molecular processes (which translate into macroscopic strain-rate and viscoelastic effects) may make measurements difficult, or less accurate, in some cases. Such time-dependent processes are most probably the reason of the low-load threshold (2–4 N) that was found in this study. No threshold was found for ceramics[4] within a wide range of loads. The correlation found in *Figure 2* between b_{rec}/a_{rec} and the Knoop hardness/modulus ratio H_k/E may not hold for materials which have substantially different recovery kinetics. Here we have limited ourselves to a range of materials that we feel are important from a practical viewpoint. For those, the correlation holds. The issue of the accuracy of the method we propose is not an easy one, and it will be addressed as more data become available. It is also possible that an experimental correlation with the yield stress exists, since for many polymers there is a link between the yield stress and the modulus. This was not pursued here as we are primarily interested in determining the elastic modulus of polymers. Another possible limitation of the method is geometrical in nature; namely, at higher

indenting loads (which are a necessity, as demonstrated here) the Knoop indentation longer diagonal may become larger than the size of the specimen. In such cases, valid tests cannot be performed. Nevertheless, the proposed method may be the only available recourse when dealing with specimens that are difficult to test otherwise, and as such it is important.

In summary, we have shown that Knoop microindentation tests may provide an estimation of the Young's modulus of polymers, provided that sufficiently high indentation loads are used. The method proposed is an extension of the procedure suggested by Marshall *et al.*[4] for ceramic materials, based on concepts proposed earlier by Lawn and Howes[1]. The approach suggested here may be particularly advantageous for the assessment of Young's modulus of small-scale polymeric regions, or when only small polymer specimens are available.

Acknowledgements

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