

A study of absolute hardness of some organic molecular solids

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Abstract : The absolute hardness is defined as the hardness number independent of the applied load. An evaluation has been made of the absolute or true hardness values for the organic solids anthracene, phenanthrene and carbazole using both the Knoop and Vickers microhardness *versus* load data. The results obtained by graphical analysis agree very well with the calculated results, within experimental error. The present note reports the results obtained, using the method utilizing the extrapolation function.

Keywords : Knoop microhardness, Vickers microhardness, organic molecular solids

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Microhardness is an important strength property of single crystals. The microhardness anisotropy of various single crystals have been studied [1-4].

For organic materials, studies have concentrated predominantly on aromatic solids because of their potential as luminescent devices [5, 6], plastic crystals due to their unique mechanical behavior [7] and organic energetic materials because of an interest in the role of dislocations in energetic decomposition processes [8].

The microhardness technique is a rapid, low cost, non-destructive method to study the deformation behavior of crystals [9]. The variation of hardness with applied load using the Vickers and Knoop indenters [10-16] has been studied earlier for the organic crystals anthracene, phenanthrene, carbazole and doped anthracene. The results have been explained on the basis of the geometrical arrangement and disposition of the molecules in the crystal structure of these solids. The results obtained from these studies have been used to derive the absolute hardness of these crystals.

Single crystals of organic molecular solids were indented on their cleavage planes using the Vickers and Knoop indenters. A

large number of indentations were made at each load and the hardness value obtained using the following relation :

$$\text{Vickers hardness } H_v = 0.02 \times P/L^2 \text{ (MPa)}, \quad (1)$$

$$\text{Knoop hardness } H_k = 0.14 \times P/L^2 \text{ (MPa)}, \quad (2)$$

where P is the applied load in g and L is the mean diagonal length in micron.

The reciprocal indentation length was plotted against hardness and a best fit straight line was drawn from the points using the Harvard graphics software [17]. This method, which utilizes an extrapolation function to determine the true hardness was developed by Tarkanian *et al* [18] and is as follows :

Let

P = applied load,

L_o = observed length of indentation,

L_t = true length of indentation under applied load,

$\Delta L = L_t - L_o$ = length correction of indentation,

C = a constant,

H_o = observed hardness,

H_t = true hardness.

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Then

$$H_0 = P / (C L_0^2) \text{ and } H_1 = P / (C L_1^2).$$

$$\text{Therefore, } H_0 L_0^2 = H_1 L_1^2. \quad (3)$$

$$\text{But } L_1 = \Delta L + L_0,$$

$$\text{hence, } H_0 L_0^2 = H_1 (\Delta L + L_0)^2.$$

$$\text{Therefore, } H_0 = H_1 (1 + \Delta L / L_0)^2. \quad (4)$$

The precision of the hardness measurements is not better than 1% so the quadratic term $(\Delta L / L_0)^2$ is neglected. If $(\Delta L / L_0) < 0.1$ then

$$H_0 = H_1 + 2 \Delta L H_1 (1 / L_0). \quad (5)$$

The correction term ΔL has been interpreted as being due to either elastic recovery [19] or optical resolution [20]. In either case, if ΔL is a constant and if the true hardness H_1 is independent of indentation size, then according to eq. (5), a plot of H_0 versus $1/L_0$ gives a straight line with an ordinate intercept H_1 and a slope $(2 \Delta L H_1)$.

The relation (5) was used to calculate the absolute hardness where H_1 = true hardness values obtained from Figures (1-3).

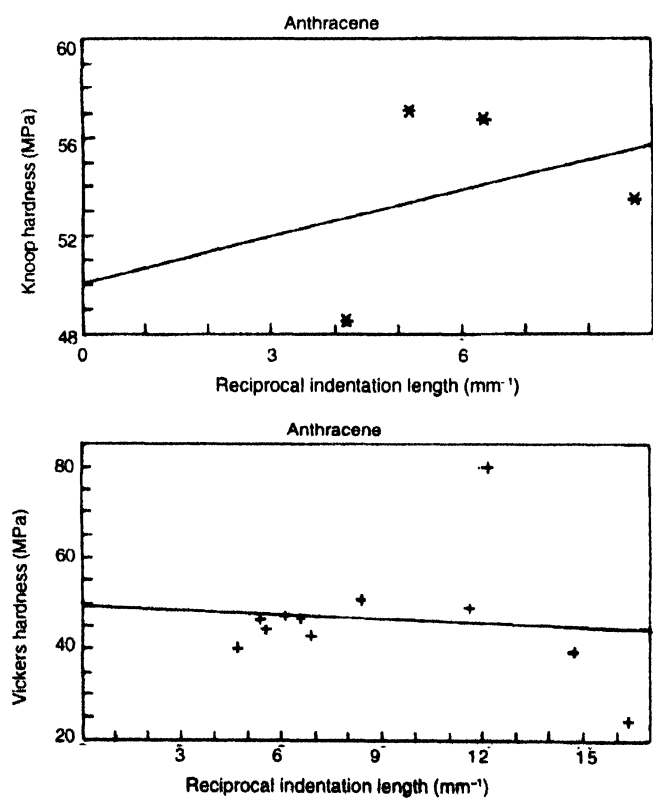


Figure 1. Reciprocal indentation diagonal length versus hardness for anthracene.

Table 1 presents the crystallographic data of the crystals studied.

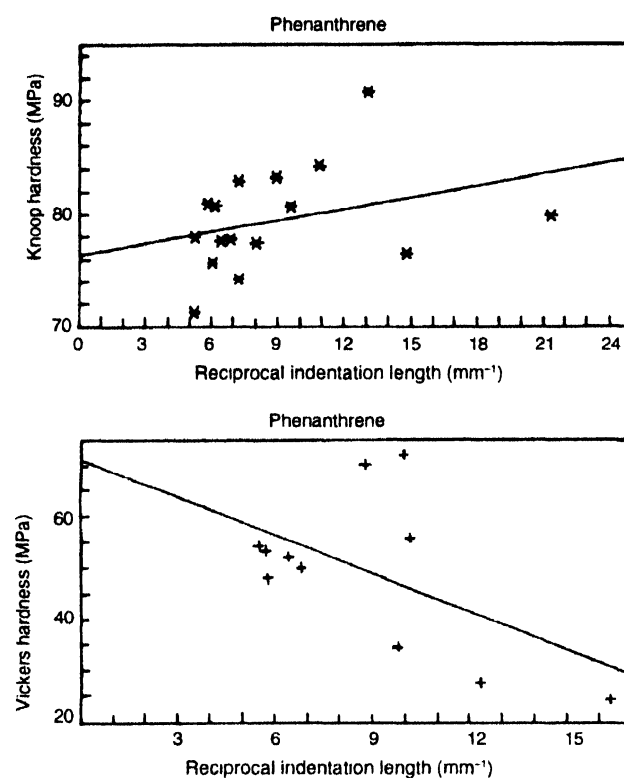


Figure 2. Reciprocal indentation diagonal length versus hardness for phenanthrene.

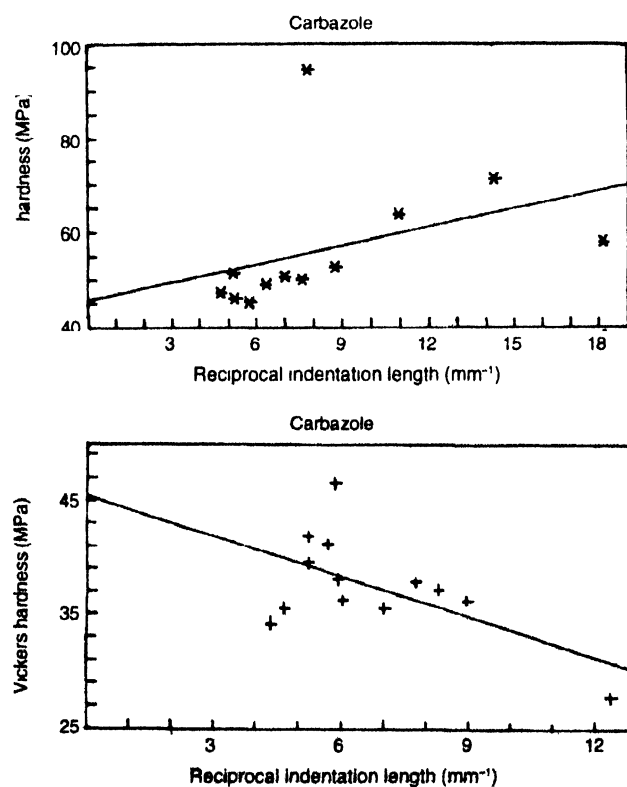


Figure 3. Reciprocal indentation diagonal length versus hardness for carbazole.

Table 1. Crystallographic data of the crystals studied

Name of the compound	Crystal system	Cleavage plane	Space group	Lattice parameters	Number of molecules per unit cell
Anthracene $C_{14}H_{10}$	Monoclinic	(001)	$P2_{1/a}$	$a = 8.562 \text{ \AA}$ $b = 6.038 \text{ \AA}$ $c = 11.184 \text{ \AA}$ $\beta = 124.11^\circ$	2
Phenanthrene $C_{14}H_{10}$	Monoclinic	(001)	$P2_{1/a}$	$a = 8.66 \text{ \AA}$ $b = 11.500 \text{ \AA}$ $c = 19.240 \text{ \AA}$ $\beta = 98.06^\circ$	2
Carbazole $C_{12}H_9N$	Orthorhombic	(010)	$P2_{2nm}$	$a = 7.772 \text{ \AA}$ $b = 19.182 \text{ \AA}$ $c = 5.725 \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$	4

Table 2 gives the results of the graphical and mathematical analysis to obtain the absolute hardness.

Table 2. The true hardness values obtained from graphical and mathematical analysis.

Compounds	H_i (Knoop) graphical (MPa)	H_i (Knoop) calculated (MPa)	H_i (Vickers) graphical (MPa)	H_i (Vickers) calculated (MPa)
Anthracene	50.10	49.55	49.0	48.74
Phenanthrene	76.40	76.36	71.50	62.61
Carbazole	45.50	46.25	45.04	45.25

Figures (1-3) depict the plots of reciprocal indentation length *versus* hardness for the crystals studied.

It is seen from the plots that the slopes of the lines using the Vickers hardness *versus* load data are opposite to that using the Knoop hardness *versus* load data. This sort of behavior could be due to change in the mode of deformation as seen from the load *versus* hardness curve where the peaks in the Vickers curve are due to the operation of the slip systems whereas in the case of Knoop indentations, it is due to splitting of a dislocation into partials. These different stress criteria can give rise to opposite anisotropies.

The absolute hardness values H_t obtained from the graphs (Figures 1-3) are used to find the length correction terms ΔL . The calculated true hardness values are found using the relations:

$$H_i \text{ (Vickers)} = 0.02 \times P / (\Delta L + L_0)^2 \text{ (MPa)}, \quad (6)$$

$$H_i \text{ (Knoop)} = 0.14 \times P / (\Delta L + L_0)^2 \text{ (MPa)}. \quad (7)$$

These values compare well with the absolute hardness values obtained graphically, irrespective of the mode of indentation, as

seen from Table 2. It is seen from Table 1 that both anthracene and phenanthrene have the same chemical formula and the monoclinic crystal structure with space group $2P_{1/a}$ and two molecules per unit cell. The packing coefficient is given by:

$$K = Z \times V_0 / V, \quad (8)$$

where V is the cell volume, Z is the number of molecules per unit cell and V_0 is the molecular volume. The packing coefficients of anthracene and phenanthrene are 0.722 and 0.684 respectively. Table 2 shows that the absolute hardness values of anthracene and phenanthrene are same within experimental error, both experimentally and theoretically using Knoop and Vickers indentation techniques. The absolute Vickers hardness value of anthracene is 49.00 MPa and that of phenanthrene is 71.50 MPa respectively as seen from the graphs 1 and 2. The higher hardness value of phenanthrene is due to the shape and molecular disposition of the molecules in the unit cell as the packing coefficients are not the same.

Carbazole crystallizes in the orthorhombic crystal structure with four molecules per unit cell and space group $P2_{2nm}$. Though the carbazole molecular shape is similar to that of the anthracene molecule, the absolute hardness value (45.04 MPa) is less than that of anthracene due to the way the molecules are dispositioned in the unit cell.

[i] It is seen from the plots that the slopes of the lines using the Vickers hardness *versus* load data are opposite to that using the Knoop hardness *versus* load data. This sort of behavior is attributed to change in the mode of deformation as different stress criteria can give rise to opposite anisotropies.

[ii] The calculated true hardness values are found to compare well with the absolute hardness values obtained graphically, irrespective of the mode of indentation.

[iii] The absolute Vickers hardness value of anthracene is 49.00 MPa and that of phenanthrene is 71.50 MPa respectively

as seen from the graphs 1 and 2. The higher hardness value of phenanthrene is due to the shape and molecular disposition of the molecules in the unit cell as the packing coefficients are not the same.

[iv] Though the carbazole molecular shape is similar to that of the anthracene molecule, the absolute hardness value (45.04 MPa) is less than that of anthracene due to the way the molecules are dispositioned in the unit cell.

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