Chapter 1

Introduction

1.1 Hardness in materials science and engineering

For about a century engineers and metallurgists have been measuring the hardness of metals as a means of assessing their general mechanical properties. How can one define the hardness of a material? An interesting remark in this respect was made by O'Neil (1967) in his introductory essay on the hardness of metals and alloys. He wisely pointed out that hardness, 'like the storminess of the seas, is easily appreciated but not readily measured'.

In general hardness implies resistance to local surface deformation against indentation (Tabor, 1951). If we accept the practical conclusion that a hard body is one that is unyielding to the touch, it is at once evident that steel is harder than rubber. If, however, we think of hardness as the ability of a body to resist permanent deformation, a substance such as rubber would appear to be harder than most metals. This is because the range over which rubber can deform elastically is very much larger than that of metals. Indeed with rubber-like materials the elastic properties play a very important part in the assessment of hardness. With metals, however, the position is different, for although the elastic moduli are large, the *range* over which metals deform elastically is relatively small. Consequently, when metals are deformed or indented (as when we attempt to estimate their hardness) the deformation is predominantly outside the elastic range and often involves considerable plastic or permanent deformation. For this reason, the hardness of metals is bound up primarily with their plastic properties and only to a secondary extent with their elastic properties. In some cases, however, particularly in dynamic hardness measurements, the elastic properties of the metals may be as important as their plastic properties (Tabor, 1951).

Hardness measurements usually fall into three main categories: scratch hardness, indentation hardness and rebound or dynamic hardness.

Scratch hardness

Scratch hardness is the oldest form of hardness measurement and was probably first developed by mineralogists. It depends on the ability of one solid to scratch another or to be scratched *by* another solid. The method was first put on a semiquantitative basis by Mohs (1882) who selected ten minerals as standards, beginning with talc (scratch hardness 1) and ending with diamond (scratch hardness 10).

The Mohs hardness scale has been widely used by mineralogists and lapidaries. It is not, however, well suited for metals since the intervals are not well spaced in the higher ranges of hardness and most harder metals in fact have a Mohs hardness ranging between 4 and 8.

Another type of scratch hardness which is a logical development of the Mohs scale consists of drawing a diamond stylus, under a definite load, across the surface to be examined. The hardness is determined by the width or depth of the resulting scratch; the harder the material the smaller the scratch. This method has some value as a means of measuring the variation in hardness across a grain boundary. In general, however, the scratch sclerometer is a difficult instrument to operate.

Static indentation hardness

The methods most widely used in determining the hardness of metals are the static indentation methods. These involve the formation of a permanent indentation in the surface of the material under examination, the hardness being determined by the load and the size of the indentation formed. Because of the importance of indentation methods in hardness measurements a general discussion of the deformation and indentation of plastic materials is given in Chapter 2.

In the Brinell test (Brinell, 1900; Meyer, 1908) the indenter consists of a hard steel ball, though in examining very hard metals the spherical indenter may be made of tungsten carbide or even of diamond. Another type of indenter which has been widely used is the conical or pyramidal indenter as used in the Ludwik (1908) and Vickers (see Smith & Sandland (1925)) hardness tests, respectively. These indenters are now usually made of diamond. The hardness behaviour is different from that observed with spherical indenters. Other types of indenters have, at various times, been described, but they are not in wide use and do not involve new principles.

Dynamic hardness

Another type of hardness measurement is that involving the dynamic deformation or indentation of the material specimen. In the most direct method an indenter is dropped on to the metal surface and the hardness is expressed in terms of the energy of impact and the size of the resultant indentation (Martel, 1895). In the Shore rebound scleroscope (Shore, 1918) the hardness is expressed in terms of

the height of rebound of the indenter. It has been shown that in this case the dynamic hardness may be expressed quantitatively in terms of the plastic and elastic properties of the metal. Another method which is, in a sense, a dynamic test is that employed in the pendulum apparatus developed by Herbert in 1923. Here an inverted compound pendulum is supported on a hard steel ball which rests on the metal under examination. The hardness is measured by the damping produced as the pendulum swings from side to side. This method is of considerable interest, but it does not lend itself readily to theoretical treatment (Tabor, 1951).

In practice, the following test methods are in use for hardness determination.

Brinell

In this test a steel ball is forced against the flat surface of the specimen. The standard method (ASTM, 1978) uses a 10-mm ball and a force of 29.42 kN. The Brinell hardness value is equal to the applied force divided by the area of the indentation:

$$HB = \frac{2P}{\pi D^2[1 - \sqrt{(1 - d/D)^2}]} \tag{1.1}$$

in which P is the force in newtons; D is the diameter of the ball in millimetres; and d is the diameter of the impression in millimetres. A 20-power microscope with a micrometer eyepiece can measure d to 0.05 mm. The minimum radius of a curved specimen surface is $2.5D$. The results of the test on polypropylene, polyoxyethylene and nylon-6,6 have been interpreted in terms of stress–strain behaviour (Baer *et al.*, 1961).

Vickers

This test uses a square pyramid of diamond in which the included angles α between non-adjacent faces of the pyramid are 136°. The hardness is given by

$$HV = \frac{2P \sin(\alpha/2)}{d^2} = 1.854\frac{P}{d^2} \tag{1.2}$$

where P is the force in newtons and d is the mean diagonal length of the impression in millimetres. The value of HV is expressed in megapascals. The force is usually applied at a controlled rate, held for 6–30 s, and then removed. The length of the impression is measured to 1 μm with a microscope equipped with a filar eyepiece (Müller, 1965). Cylindrical surfaces require corrections of up to 15% (ASTM, 1978).

Knoop

Another commonly used hardness test uses a rhombic-based pyramidal diamond with included angles of 174° and 130° between opposite edges. The hardness is given by

$$HK = C\frac{P}{d^2} \tag{1.3}$$

where P is the force in newtons, d is the principal diagonal length of indentation in millimetres and C is equal to 14.23 (ASTM, 1978). The Vickers test gives a smaller indentation than the Knoop test for a given force. The latter is very sensitive to material anisotropy because of the twofold symmetry of the indentation (Baltá Calleja & Bassett, 1977).

Rockwell

In this test the depth of indentation is read from a dial (ASTM, 1978); no microscope is required. In the most frequently used procedure, the Rockwell hardness does not measure total indentation but only the non-recoverable indentation after a heavy load is applied for 15 s and reduced to a minor load of 98 N for 15 s. Rockwell hardness data for a variety of polymers are reported by Maxwell (1955) and Nielsen (1963).

Scleroscopy

In this test the rebound of a diamond-tipped weight dropped from a fixed height is measured (Maxwell, 1955; ASTM, 1978). Model C (HSc) uses a small hammer (*ca* 2.3 g) and a fall of about 251 mm; model D (HSd) uses a hammer of about *ca* 36 g and a fall of about 18 mm.

Scratch hardness

This test measures resistance to scratching by a standardized tool (ASTM, 1978). A corner of a diamond cube is drawn across the sample surface under a force of 29.4 mN applied to the body diagonal of the cube, creating a V-shaped groove; its width Λ, in micrometres, is measured microscopically. The hardness is given by:

$$HS = 10\,000/\Lambda \tag{1.4}$$

The constant 10 000 is arbitrary.

Applicability of the tests

The Vickers and Brinell hardness scales are almost identical up to a Brinell hardness of about 5 GPa. This range covers all polymeric materials. The Brinell test is preferred for measuring the macrohardness of large pieces in which a large indentation (2.5–6 mm diameter) is acceptable. The Vickers macrohardness test ($P > 30$ N) is used mainly where the indentation is limited in size. The Vickers microhardness test ($P < 1$ N) is used mainly with small and inhomogeneous specimens. Forces down to 10 mN are suitable for most commercial instruments. There are testers that can operate down to 10 μN in conjunction with a scanning electron microscope (Bangert *et al.*, 1983). The Knoop microhardness test is more rapid than the Vickers test and more sensitive to material anisotropy. The Rockwell instrument is used in production and quality control where absolute hardness is unimportant. The scleroscope is used for specimens that cannot be removed or cannot tolerate large indentations. Values given by the scleroscope (dynamic hardness) and the

static-ball indenter correspond directly. The scratch test is used where indentation microhardness tests cannot be made close enough to determine local variations. Typical microhardness values for polymers are summarized by Boor (1947).

1.2 Microhardness in polymer science

1.2.1 Microhardness and deformation modes in polymers

The microhardness (H) of ionic and metallic crystals and polycrystalline specimens has been extensively investigated (Kuznetsov, 1957; Brookes *et al.*, 1971, 1972; O'Neil *et al.*, 1973). In these materials microhardness is essentially determined by primary slip systems which involve dislocation movements during the indentation process. In molecular (paraffinic) crystals on the other hand, typical deformation modes preferentially include displacement of the chains by shearing and tilting and eventually twinning and phase transitions (Baltá Calleja, 1976). Crystal defects (dislocations, kinks, vacancies, and so on) facilitate such a deformation but are overwhelmingly dominated by the anisotropy of mechanical forces: namely, strong covalent bonding in the chain direction and weak van der Waals forces normal to it. Thus, in low-molecular-weight materials, as a consequence of the large anisotropy of the crystal force field crystals are relatively weak, exhibiting very poor mechanical properties. Knoop indentations on the (001) planes of solution crystallized paraffin single crystals ($n = 32$–44) are often accompanied by the development of ridges along specific crystallographic directions (Baltá Calleja, unpublished). The occurrence of these roof shaped ridges implies a change from a vertical to an oblique structure as shown by Keller (1961), thus suggesting a shearing of the molecules in the ($hk0$) slip planes as one of the possible modes of plastic deformation, frequently leading to the observed final macroscopic fracture of the crystals.

The study of microhardness in polymers, in its earliest stages, was mainly restricted to applications of technological interest (Holzmüller & Altenburg, 1961; Nielsen, 1963), such as the determination of macroscopic internal stresses in the surface of plastics (Racké & Fett, 1971). The study of microindentation offers the specific advantage of being a local deformational process restricted to depths of a few micrometres thus leaving unaltered, in contrast to bulk deformation, the rest of the test sample. Since the indentation process is primarily controlled by plastic deformation (Brookes *et al.*, 1972) the microhardness value will be intimately correlated to the specific modes of deformation operative in polymers. In these macromolecular solids, one cannot explain the observed mechanical properties on the sole basis of crystal lattice and defects. The deformation modes in the crystalline polymer are predominantly determined by the arrangement and structure of the microcrystalline domains and their connection by tie molecules. The crystals restrict the mobility of the molecules in the amorphous layers, while the latter partly

transmit the required forces for the break up of crystals and additionally provide for elastic recovery when the local stress field is removed (Hosemann *et al.*, 1972; Peterlin, 1987).

1.2.2 Microhardness additivity law

It is important to note in these introductory remarks that, like many mechanical properties of solids, microhardness obeys the additivity law:

$$H = \sum_i H_i w_i \tag{1.5}$$

where H_i and w_i are the microhardness and mass fraction, respectively, of each component and/or phase. This law can be applied to multicomponent and/or multiphase systems provided each component and/or phase is characterized by its own H. Equation (1.5) is frequently used in semicrystalline polymers for one or other purpose operating with the microhardness values of the crystalline H_c and amorphous H_a phases, respectively.

Application of the additivity law (eq. (1.5)) presumes a very important requirement – each component and/or phase of the complex system should have a T_g above room temperature, i.e. it should be a solid at room temperature and thus capable of developing an indentation after the removal of the indenter. If this is not the case, the assumption $H = 0$ for the soft component and/or phase does not seem to be the best solution, although it is frequently done.

The presence in a complex system of a very soft, liquid-like component and/or phase (not having a measurable H value at room temperature) can affect the deformation mechanism of the entire system in such a way that it does not obey the additivity law (eq. (1.5)). This situation is discussed in more detail in the subsequent chapters.

1.2.3 Tabor's relation

Another motivation for measurement of the microhardness of materials is the correlation of microhardness with other mechanical properties. For example, the microhardness value for a pyramid indenter producing plastic flow is approximately three times the yield stress, i.e. $H \sim 3Y$ (Tabor, 1951). This is the basic relation between indentation microhardness and bulk properties. It is, however, only applicable to an ideally plastic solid showing no elastic strains. The correlation between H and Y is given in Fig. 1.1 for linear polyethylene (PE) and poly(ethylene terephthalate) (PET) samples with different morphologies. The lower hardness values of 30–45 MPa obtained for melt-crystallized PE materials fall below the H/Y *ca* 3 value, which may be related to a lower stiff–compliant ratio for these lamellar structures (Baltá Calleja, 1985b). PE annealed at *ca* 130 °C

($H \sim 75$ MPa) gives an H/Y ratio closer to that predicted for an ideal plastic solid. Thus plastics showing a high stiff–compliant ratio (high-crystallinity) approach the $H/Y \sim 3$ relation, whereas those with a low stiff–compliant ratio (low crystallinity) deviate from the classical plasticity theory. In PET samples one observes a similar behaviour. The mechanical properties (H, Y) improve when passing from the amorphous to the crystalline state. Smaller values for the H/Y ratio are obtained when the strain rate of the tensile test is much larger than that used in the indentation test (Baltá Calleja *et al.*, 1995). Values smaller than $H/Y = 3$ are also found when using the yield stress in compression (Flores *et al.*, 2000). This is due to the fact that $Y_{compression}$ is larger than $Y_{tension}$. The difference has been ascribed to the effect of the hydrostatic component of compressive stress on isotropic polymers including PE (Ward, 1971) (see Chapter 4).

An experimental relationship between the microhardness and elastic modulus (E) has been found for various PE materials with different crystallinity values (Flores *et al.*, 2000). It is important to realize that microhardness – the plastic deformation of crystals at high strains – primarily depends on the average thickness and perfection of the nanocrystals, whereas in the case of the modulus, the elastic response at low strains is dictated by the cooperative effects of both microphases, the crystalline lamellae and the amorphous layer reinforced by tie molecules. The

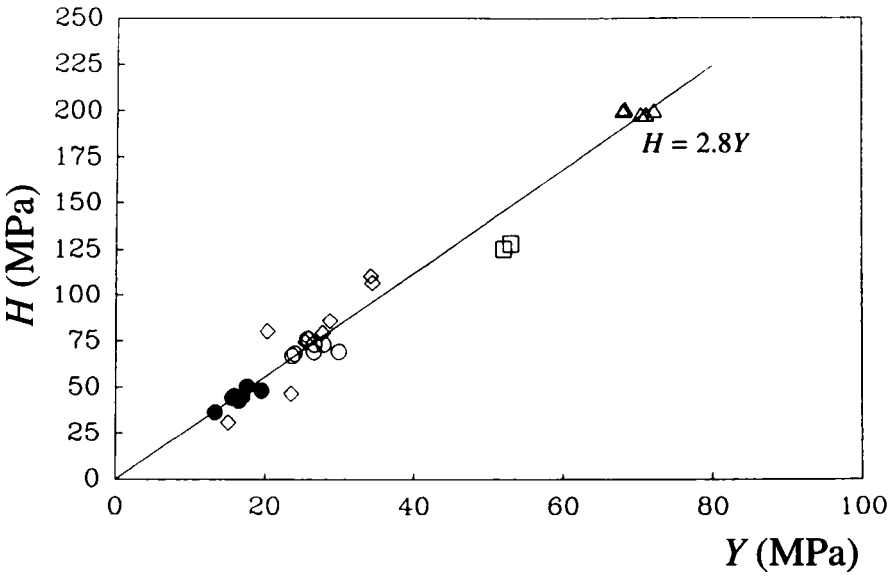

Figure 1.1. Correlation between hardness at 6 s (loading time) and yield stress of PE and PET samples with different crystallinities: (●) quenched PE at −84 °C; (○) PE slowly cooled at 4 °C min^{-1}; (◇) PE annealed at atmospheric and at high pressure (4 kbar); (□) glassy PET; (△) crystallized PET. (From Santa Cruz, 1991.)

microhardness increase modulated by the chain extension of the crystals usually parallels the increase in stiffness. However, the specific dependence of H upon E for the different morphological units, gives rise to a different dependence of H upon E in systems where the rubber elastic behaviour of the amorphous layers is more pronounced (Baltá Calleja & Kilian, 1985).

1.2.4 Microhardness of polymers in contrast to metals

The common belief that a crystalline solid is always harder than an amorphous one, regardless of the chemical composition, seems to be misleading. This has been demonstrated on gelatin films (Fakirov *et al.*, 1999). This commodity polymer, known as a very soft product in the gel state, turns out to have a very high hardness value even at elevated temperatures (150–200 °C) provided it is measured in the dry state. Its microhardness of 380–400 MPa (at room temperature with 10–15% water content, H is around 200 MPa) surpasses that of all commonly used commercial synthetic polymers and some soft metals and alloys, as can be concluded from Fig. 1.2.

Paraffins, PE and metals, such as Pb and Sn, have microhardness values below 100 MPa. Semicrystalline polyoxymethylene, PET, chain-extended PE, poly(ethylene 2,6 naphthalate) and metals, such as Al, Au, Ag, Cu and Pt, have values between 100 and 300 MPa. The microhardness values of carbon-fibre-reinforced polymer composites are about 900 MPa and those for the common metals Zn and Co are 2000 and 4000 MPa, respectively, while for white steel it is 5000 MPa.

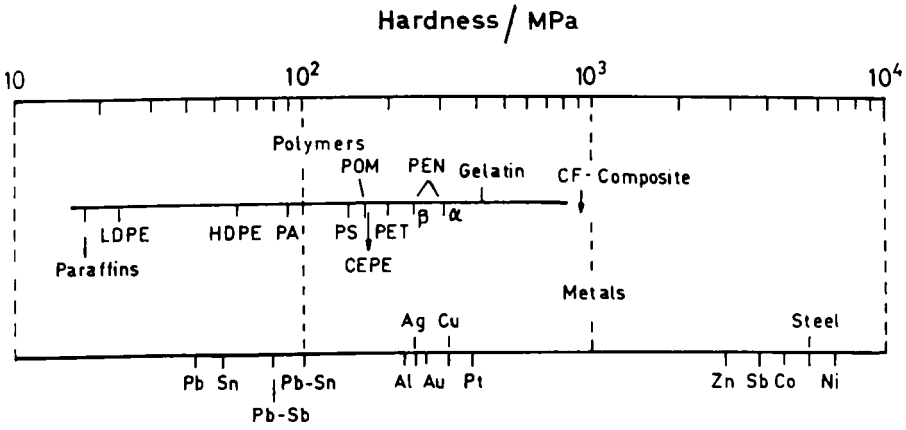

Figure 1.2. Typical microhardness values of polymers compared with data for metals. LDPE, low-density polyethylene; HDPE, high-density polyethylene; PA, polyamides; POM, polyoxymethylene; CEPE, chain-extended polyethylene; CF-composite, carbon-fibre composite; PS, polystyrene; PEN, poly(ethylene naphthalene-2,6-dicarboxylate. (From Baltá Calleja & Fakirov, 1997.)

The microhardness of thermally untreated gelatin of 400 MPa surpasses that of all commonly used synthetic polymers and soft metals and the value for the thermally treated gelatin of almost 700 MPa (Vassileva *et al.*, 1998) approaches that of the carbon-fibre-reinforced composites.

The fact that gelatin is distinguished by such a high microhardness value when in the amorphous state has another important advantage. It is known that amorphous solids are structurally ideal, i.e. they are free from structural defects unlike crystalline solids, and for this reason they have superior barrier properties.

In conclusion, let us emphasize some areas of polymer research that offer new possibilities for applications of the microindentation method to measurements of the mechanical properties of polymer surfaces. These include further microhardness–morphology correlations of flexible and rigid crystallizable polymers, microfibrillar materials and non-crystallizable glasses. Researchers interested in surface properties will recognize future opportunities in the characterization of ion-implanted polymer surfaces, coatings and weathering characterization of polymeric materials (see Chapter 7). Of particular interest is the applicability of the technique to new high-tech materials characterized by extremely high surface microhardness. Finally, it is expected that nanoindentation techniques will offer novel possibilities for studying the elastic and plastic properties of the near-surface region of polymers.

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