On the Relationship Between Modulus of Elasticity and Microhardness

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ABSTRACT: The correlation between the modulus of elasticity, on the one side, and Vickers microhardness and total microhardness, on the other side, was analyzed in the case of ultrahigh molecular weight polyethylenes. An extension of the application of the power relation between microhardness and the modulus ($MH = aE^b$) obtained by different methods was suggested. A linear dependence between constants obtained by Vickers and total microhardness measurements and other different techniques of modulus measurement was established, which signifies that both microhardness characteristics change their sensitivity toward the modulus in a similar way. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1794–1798, 2003

Key words: modulus; hardness; polyethylene; mechanical properties; indentation

INTRODUCTION

Microhardness is not only a mechanical characteristic routinely measured, but, in recent years, it has been developed as an investigation method because it has been established that it is sensitive to structural parameters as well as to mechanical behavior (yield stress, modulus of elasticity, some secondary relaxation transitions, etc.[1–6]). Therefore, this micromechanical characteristic plays the role of a connecting link between the structure and macromechanical properties. The relation between microhardness and other mechanical properties was established and applied at the beginning for metals, because of their better-investigated structure and mechanical properties, and during the last 15 years, it was extended to polymers. The connection of microhardness with the modulus of elasticity has a physical reason because both of them depend on the material structure and the corresponding intramolecular and intermolecular interactions. The dependence early proposed by Baltá-Calleja[1] for semicrystalline polymers, later confirmed by the experimental results for polyethylenes,[7] and for copolymers of ethylene-α-olefins[8,9] is a power relation between Vickers microhardness (MHV) and the modulus of elasticity (E) obtained by tensile stress–strain measurements:

$$MHV = aE^b \quad (1)$$

where a and b are constants.

In one of the most recent reports about the relation between the elastic modulus and microhardness concerning highly oriented polyethylene samples, a proportional dependence was proposed[10]:

$$MHV \approx E/10 \quad (2)$$

This suggestion was based on Tabor's relation[11] and Struik's model,[12] which predicts a proportional dependence between yield stress and the modulus of elasticity. Struik's model was founded on general considerations about the relationships between the bond energy and the mechanical properties.

Also, a technique for measuring microhardness and the modulus, based on the assumption that the elastic recovery in the depth of the Vickers indentation is proportional to the ratio MHV/E, was developed.[13] Moreover, a semiempirical linear relationship between the extent of the elastic recovery of the diagonals of a Knoop indenter and the ratio of the modulus of elasticity to the hardness was proposed[14] and experimentally demonstrated, first for ceramics[14] and later for polymeric materials.[15]

Dedicated to Professor Ricardo Granados on the occasion of his 85th birthday.

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TABLE I
Molecular Masses and Crystallinity Degrees of the UHMWPE Samples

Sample no.	Catalyst system	$M_\eta \times 10^6$	$F_c^{x\text{-}ray}$ (%)
1	V/SiO_2	5.4	60
2	Ti/SiO_2	2.1	66
3	Ti/SiO_2	1.0	72

Knowledge of the dependence between the modulus of elasticity and the microhardness allows the estimation of the elastic modulus of small specimens, which is impossible to do with other common approaches. Moreover, although microhardness is an indirect technique, it is also a fast, simple, and easy-to-measure nondestructive method.

The aim of the present work was to study the validity for ultrahigh molecular weight polyethylene (UHMWPE) of the previously proposed relation (1) between Vickers microhardness and the modulus of elasticity. An estimation of the possibility for extending these relations to values of the modulus obtained by different methods—ultrasound (US) and dynamic mechanical (DMTA) measurements—was also an object of study, to establish a wider applicability of those relations. The relation between the total microhardness (*MHT*), a microindentation characteristic governed by general deformational properties of the material,[16] and the moduli obtained at different measuring frequencies was also an objective of the present investigation.

EXPERIMENTAL

Materials

Three types of semicrystalline UHMWPE, obtained with amorphous SiO_2-supported Ziegler–Natta catalyst systems modified by vanadium (sample 1) and titanium (samples 2 and 3), were used as well-defined experimental samples for different microhardness and elastic modulus measurements. Table I shows the main characteristics of the samples, which were previously characterized and studied using other techniques.[17,18]

Microhardness measurements

Microhardness characterizes the local resistance of a material against penetration of a harder body with a special shape called an indentor. The most popular and frequently used microhardness characteristic is Vickers microhardness, *MHV*, where the indentor is a regular square-based diamond pyramid, with top angle of 136°, and it is determined according to the equation

$$MHV = 2 \sin 68^\circ P/d^2 \quad (3)$$

where d is the projected diagonal length of the imprint after releasing the indentor and P is the applied load. The Vickers microhardness is connected with the permanent deformation properties of the material.

The total microhardness, *MHT*,[16] was also determined according to a similar equation:

$$MHT = KP/D^2 \quad (4)$$

where D is the projected diagonal length of the indentation in the loaded state. Thus, this defined value can be considered as a measure of the total material resistance against penetration, including elastic, plastic, and viscoelastic components.

Loads ranging from 1.25 to 160 g were used. The measuring equipment was a Vickers microhardness device mhp-160 attached to a microscope UN-2.

Stress–strain tensile measurements

Stress–strain measurements at a tensile rate of 2.5 min^{-1} were carried out with an MT205 Debewn Microtest testing module. The modulus of elasticity was determined from the slope of the initial linear part of the stress–strain dependencies. The reported results are the average of three measurements and the confidence interval (confidence level = 95%) is close to 5% of the central value.

DMTA measurements

Dynamic mechanical measurements were carried out with a Polymer Laboratories MK II dynamic mechanical thermal analyzer working in the tensile mode. The values of the elastic modulus at 22°C were determined from the temperature dependence of the dynamic storage modulus, E'. Measurements were provided at frequencies of 1, 3, 10, and 30 Hz.

Ultrasound measurements

A standard ultrasound defectoscope USIP11 was used for the ultrasound measurements. The method consists of the determination of the speed of a longitudinal ultrasound wave in the reflection mode. The ultrasound wave frequency is 4 MHz. Actually, it is measured by the time needed by the wave to pass the distance $2l$, where l is the thickness of the sample investigated. The accuracy of the time measurements is in the order of 0.02 ms.

To calculate the elastic modulus, well-established dependencies between the mechanical characteristics of the investigated material and the speed of the longitudinal ultrasound waves were used[19]:

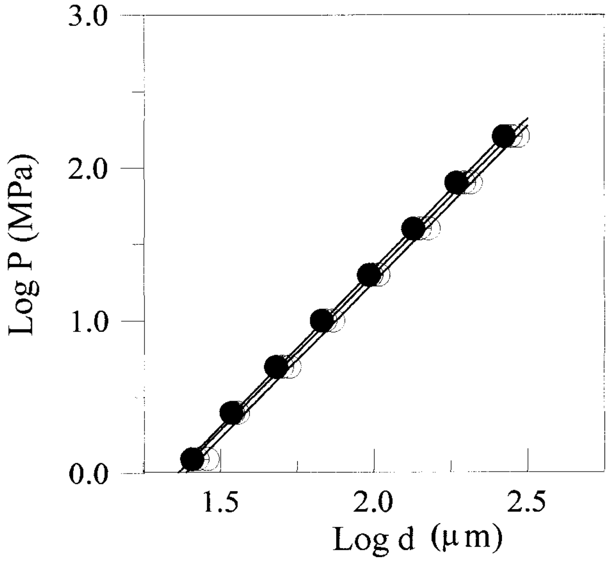

Figure 1 Mayer's lines (logarithmic dependence between applied load, P, and diagonal of the indentation, d).

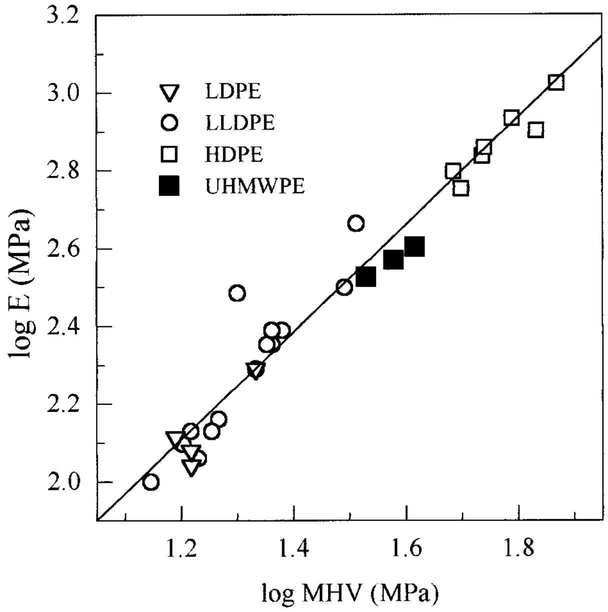

Figure 2 Logarithmic dependence of microhardness versus modulus of elasticity obtained by stress–strain experiments. Line and open symbols are according to ref. 7. The UHMWPE measured in this work is marked with filled squares.

$$E = \frac{(1 + \mu)(1 - 2\mu)}{\mu} \rho c_l^2 \qquad (5)$$

where E is the acoustic elastic modulus; ρ, the density of the medium; μ, the Poisson's ratio; and c_l, the speed of the longitudinal ultrasound waves. The value of 0.35 for the Poisson's ratio and 1.05 g/cm^3 for the density, measured picnometrically, were used for the calculations.

RESULTS AND DISCUSSION

Figure 1 shows the Mayer's lines for the three types of UHMWPE investigated. The Mayer's lines are the logarithmic expression of Mayer's power law:

$$\log P = \log m + n \log d, \qquad (6)$$

where P is the applied load; d, the projected diagonal length of indentation; and m and n, physical parameters corresponding to strength and plastic properties, respectively. The controlling of the limits of applicability of Mayer's power law guarantees the reliability of the obtained Vickers microhardness results.

The good correlation coefficients of the straight lines (r = 0.9994–0.9998) (Fig. 1) confirm the potential relation between the applied load, P, and the diagonal indentation, d, in the investigated load range (from 1.25 to 160 g). The same approach was applied for relations among the applied load, P, the projected diagonal length of the indentation in the loaded state, D, and the total microhardness.

It was established that Mayer's power law is valid only for loadings greater than 10 g (r = 0.9960–0.9969). This restriction of applicability of the power law for indentations under that load is because, at smaller loads, the part of the elastic and viscoelastic components of deformation prevails and the plastic one is relatively smaller.

Our results are plotted in Figure 2 together with those previously reported by Lorenzo et al.[7] It can be seen that the results corresponding to the UHMWPE samples can be explained in terms of the same phenomenological expression that describes the ones corresponding to linear and branched polyethylenes and

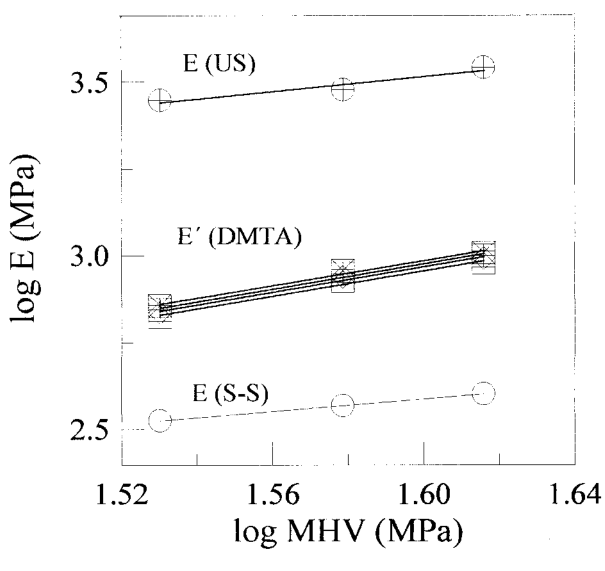

Figure 3 Elastic modulus obtained by different methods (tensile test S–S, DMTA, and US) as a function of Vickers microhardness, MHV.

TABLE II
Values of the Constant b of Eq. (1) for Different Methods and Frequencies

Method	Frequency (Hz)	$b_{(MHV)}$	$b_{(MHT)}$
S–S	~0.05	1.113	1.664
DMTA	1	0.550	0.844
DMTA	3	0.547	0.840
DMTA	10	0.549	0.843
DMTA	30	0.559	0.856
US	4×10^6	0.936	1.314

ethylene–α-olefins copolymers, irrespective of the different lengths and structures of their macromolecular chains. Even more, it can be concluded that the microhardness and elastic moduli of the new UHMWPE samples occupy an intermediate position between LLDPE and HDPE. This result points to the fact that we are only considering a relationship between mechanical properties of materials of which the microscopic mechanisms of plastic and elastic deformations are very similar.

Figure 3 compares the values of the elastic modulus obtained by different methods [tensile stress–strain test (S–S), dynamic mechanic thermal analysis (DMTA), and ultrasound testing (US)] as a function of Vickers microhardness, *MHV*. The values of the modulus increase exponentially with increasing of the microhardness, which is in accordance with the above-commented eq. (1), and the values of coefficient b are specific for the method of modulus determination (Table II).

The same approach was used for determining the relationship between total microhardness, *MHT*, and modulus of elasticity obtained by different methods (Fig. 4). Again, very similar exponential dependencies are obtained.

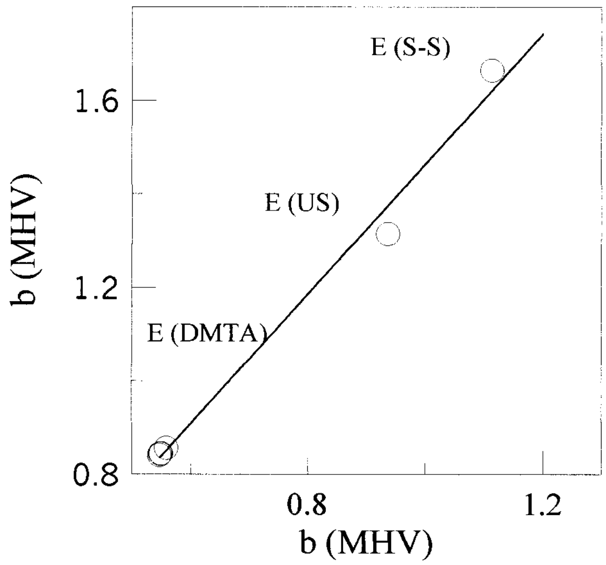

Figure 5 Dependence between b constants obtained from the exponential dependencies $MHV = f(E)$ and $MHT = f(E)$.

Figure 5 illustrates the linear dependence between b constants obtained from the exponential dependencies $MHV = f(E)$ and $MHT = f(E)$. Taking into account that values of b express a power dependence of the microhardness on the modulus, it could be concluded that the constant b could be considered as an indicator of the microhardness sensitivity toward the modulus of the elasticity. The highest b values correspond to the moduli obtained by S–S tensile measurements, followed by ones obtained by US and DMTA measurements. Therefore, the sensitivity of the microhardness to the modulus obtained by S–S measurements is the

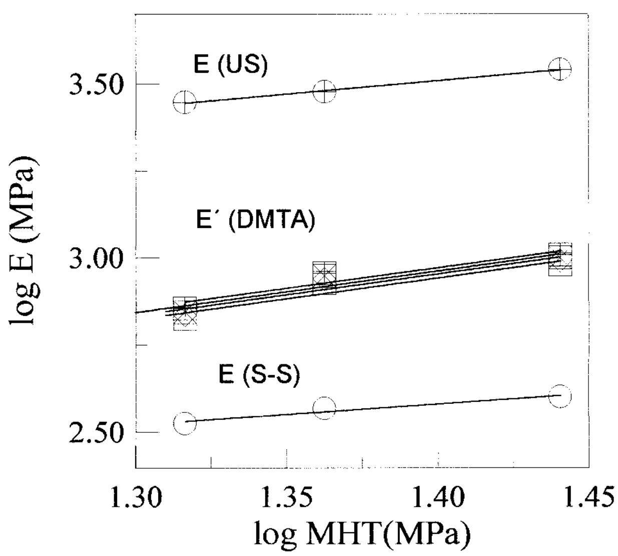

Figure 4 Elastic modulus obtained by different methods as a function of total microhardness, *MHT*.

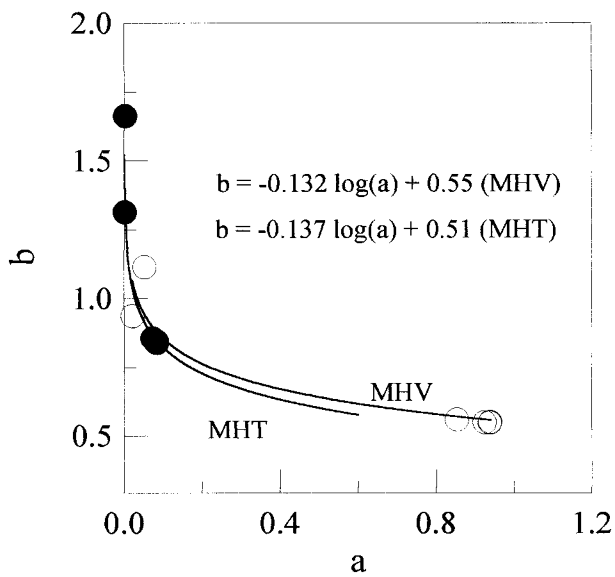

Figure 6 Dependence between constants a and b from eq. (1) for the different combinations of the *MH–E* relations.

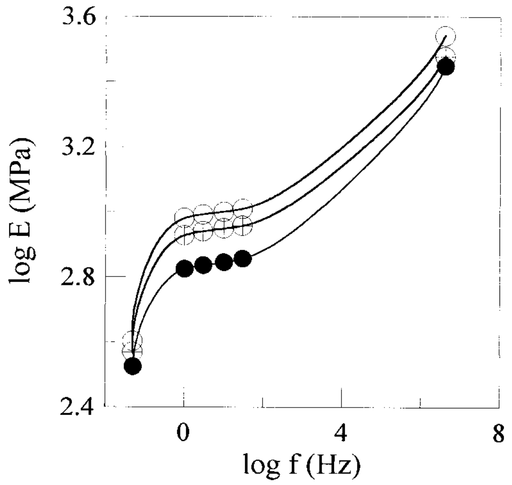

Figure 7 Elastic modulus as a function of frequency for the three samples, measured using different techniques.

greatest one, which signifies that the usual accepted practice to compare *MHV* with $E_{S\text{–}S}$ is the most precise way to do it.

The values of the constant *b* from the relation (1) are higher for the *MHT–E* dependencies in comparison with the *MHV–E* ones, and the linearity of the $b_{MHT} - b_{MHV}$ dependence shows that both microhardness characteristics (*MHV* and *MHT*) change their sensitivity toward *E* in the same way. Moreover, Figure 6 shows that the changes in the values of constants *a* and *b* from eq. (1), in the different combination of the *MH–E* relations, lead to a dependence of the type

$$b = -k \log a + k' \tag{7}$$

where the constants k and k' are very close for both microhardness methods used.

A further confirmation of the results of this article can be deduced from the trend of the variation of the elastic modulus as a function of frequency (Fig. 7), obtained by means of the various types of *E* measurements carried out at different frequencies. Regardless of some simplifications (the frequency of the S–S tensile measurement was assumed to be 0.05 Hz), that trend parallels the shape of the classical dependence of the modulus on the frequency in the glassy region of polymers (see, for instance, ref. 20).

CONCLUSIONS

1. An extension of the application of the relation $MHV = aE^b$ to moduli obtained by different methods and to total microhardness is suggested. The values of constants *a* and *b* for UHMWPE were experimentally obtained.
2. A linear dependence between constants *b* obtained by *MHV* and *MHT* measurements and different *E* measurements was established, which signifies that both microhardness characteristics change their sensitivity toward the elastic modulus obtained by different methods in the same way.
3. The change of the values of the constants *a* and *b* in different *MH–E* relations follows an exponential dependence.

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