ENGINEERING MECHANICS 2009
National Conference with International Participation
Svratka, Czech Republic, May 11 – 14, 2009

pp. 1481–1487
Paper **#284**

INFLUENCE OF OWN HARDNESS OF THE SUBSTRATE ON THE MICROINDENTATION MEASUREMENT OF THIN POLYMER MATERIALS

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Summary: *Various microindentation approaches to determining the real mechanical properties of thin polymer materials are presented. The advantages and disadvantages of these methods and the limits to their application are discussed.*

1. Introduction

Untill recently, microhardness was considered to be a standard routinely measured mechanical characteristics. Nowadays, microindentation experiments are being developed as a method for materials investigations. Unfortunately the standard method for determining Vickers microhardness (MHV) based on indentations of the diagonals after indenter extraction is not applicable to studies on thin materials such as foils and polymeric coatings. In most cases, microindentation data is distorted by the own mechanical properties of the substrate.

The aim of this work is to list and discuss the known methods for determining the microhardness of *thin* materials developed for metals and alloys. We also report on the limits of their application for thin polymer materials estimate by our investigations on polymer foils and coatings.

The basic methods are:

1. Vickers microhardness (MHV) and other methods based on the imprint of the hard indenter which according to its shape may be of Brinel, Knoop, Bercovitch etc. type.
2. Total microhardness (MHT) (Zamfirova, Dimitrova (2000));
3. Microhardness profiles (MHV=f(h) ; MHT=f(h); MHV=f(P); MHT=f(P), where P is the applied load and h is the depth of indentation in the loaded state.)
4. The Osterley graphical interpolation method (IHV)
5. Relative hardness measured by a free pendulum
6. The Sclerometric Method
7. Nanoindentation

Attention will be paid mainly to the first four methods.

2. Experimental

The materials studied are LDPE foils of various thicknesses (20, 40, 80, 100μm). The substrate material was chosen to be of different hardnesses: steel, LLDPE and rubber for the microhardness profile experiments, and brass and cardboard for the measurements with a free pendulum. The measurements were carried out on a mhp-160 type tester attached to a UN-2 microscope, and on device with a free pendulum.

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3. Results and discussion

Microhardness differs from hardness and depends on applied load and on the size of the imprint, respectively.

3.1. Vickers microhardness is a physical parameter characterising local material resistance against plastic deformation during penetration of a pyramidal indenter into the material. This characteristic is related to the irreversible, component of deformation and is calculated according to the formula:

$$MHV = kP/d^2, \quad (1)$$

Where k is a constant depending to pyramid geometry, P is applied load d is the average length of the diagonal left by the indenter. As the PE foil is relatively elastic in some cases Vickers microhardness measurements are not precise.

3.2. Total microhardness (MHT) is a microindentation characteristic based on the dimensions of the imprint in loaded state. (Zamfirova, Dimitrova 2000) MHT is more important because gives a rather different information about the material structure and its mechanical properties. It is calculated by the analogy of Vickers microhardness:

$$MHT = kP/D^2, \quad (2)$$

where D is the is the diagonal length in loaded state. Thus defined this characteristic can be considered as a measure for the local total material resistance against penetration and is connected with total deformation, including elastic, plastic and viscoelastic components. Together with MHV it gives information about the elasticity of the material and tentative information about the properties of the amorphous phase.

3.3. Microhardness profiles which are sensitive to non-uniformity of the structure in the depth of the sample. **(**Baleva et al., 2000) Microhardness profiles are dependences of Vickers microhardness and Total microhardness on the applied load (P), respectively, on the penetration depth (h):

$$MHV=f(P);\ MHV=f(h);\ MHT=f(P);\ MHT=f(h) \quad (3)$$

Noteworthy is that if MHV and MHT, respectively, are determined when indenter penetrates till the depth (h), the value does not correspond to the real microhardness exactly in this depth. This value includes microhardness properties of all layers situated between the surface and this depth. Usually the MHT slightly and uniformly increases with the increasing load. This experimental fact could be explained by the increase in the resistance against the penetrating indenter similar to the action of the compressing spring. The slope of this part of curves roughly correlates with the module of elasticity. The higher module possesses the material the more steeper is this curve. This method is also suitable for characterization of laminated materials and coatings or for tracing the changes in the structure and properties of the surface layer upon chemical, physical or mechanical treatment.

When the Vickers microhardness or Total microhardness of thin samples was measured, two principal distortions could be observed:

At a higher applied load on the indenter, the substrate itself influences the hardness data. As the substrate is usually a hard material, the microhardness values become higher than the real values. Microhardness standards usually require the relation between sample thickes and indentation depth (L/h) to be more than 10, in order to minimize the influence of the substrate. Our previous measurements on a varnish coating based on chlorine rubber and ethylcellulose showed that the softer the material, the smaller is the relation L/h (for chlorine rubber MHV≈10MPa, L/h >2; for ethylcellulose MHV≈70MPa L/h >5).(Zamfirova, G. 1988) (When

the experimental error is considerable direct MHV and MHT measurements are limited to small loads.

At a lower applied load on the indenter, the microhardness increases abnormally. There is until no uniform opinion about the physical nature of this phenomenon. Some authors have attributed it to imperfection of the pyramid top. Others consider it as a manifestation of the scale factor connected with the concept that the real material structure includes various imperfections. In the surface layers the imperfections could be of two types according their origin: defects which are characteristic for the material and exist in all its volume and other that appear only in surface layers as a consequence of a technological process or ageing.

How these defects influence microhardness measurement?

In general scale factor is the influence of the dimension and the geometry of the samples on their mechanical properties. There are various theories and hypothesis related to the physical nature of the scale factor, among them is the better known statistic theory. According to this theory scale factor could be manifested in microhardness measurements, if defects number under the indenter is small. So, the smaller is the indent, the smaller is the probability Vickers pyramid to get through a defective area. Then measured experimental microhardness values are close to those of the perfect structure. To be sure that abnormal microharness increases at small loads is due to scale factor manifestation one should evaluate the experimental errors, which in this case increase significantly.

The method suggested by Bukle (1973) allows to avoid the distortions appearing at lower and higher applied load. It consists of applying the additive law to the couple coating/substrate.

$$H_{cs}=\alpha H_c +(1- \alpha) H_s \quad (4)$$

where H_{cs} is the microharness of the couple under investigation, H_s is substrate microhardness, H_c is the coating microhardness and α is a coefficient dependent on the film thickness (L). According to Baleva at al. there is a physical reason to express the coefficient α as a sigmoidal function of a penetration depth (h).

$$\alpha = [1-\exp((h-L)/ \Delta L)]^{-1} \quad (5)$$

where, h is the depth of indentation, and increment ΔL is the dimension of the transition region (also depending on the surface state, i.e. smoothness and elastic properties of both phases) (Baleva et al., 2000)

If $h < L$ (small indentation) the dependence $\alpha(h)$ tends to *1* and $1-\alpha(h)$ tends to *0*. In this case when measuring the couple coating /substrate, the contribution of proper microhardness of the coating predominates.

If h is relatively hogh, the indenter comes up to the substrate or even at larger indentation could penetrate the substrate. The dependence $\alpha(h)$ tends to *0* and $1-\alpha(h)$ tends to *1*. In this case when measuring the couple coating /substrate, the contribution of proper microhardness of the substrate predominates.

In this manner the microhardness of a foil or coating materials could be calculated even in the cases when direct measurements of the MHV, MHT and microhardness profiles are distorted by substrate influence.

In the following figures are given the application of this method for measurement of PE foils with different thickness and on substrates with different hardness. All experimental data for the substrate are marked with quadrangles, for couple thin material/substrate with circles and calculated data for the thin material with dark triangles.

Fig.1 shows the MHV profiles versus applied load for PE foils with 20μm thickness on the steel substrate. The MHV values for steel show abnormal augmentation at small loads, while for couple there is not. Perhaps it is due to the of the scale factor because at same applied load the imprint dimensions are mach smaller in the steel than in the polymer material, thus the probability for its reviling gets greater. At loads higher than 40g substrate influence is already noticeable. Because PE foils MHV are very elastic measurements were difficult. The other measurements concern MHT profiles.

Fig. 2 demonstrates the MHT profiles for the same couple as a fig. 3. As seen for thin foils the values of proper MHT microhardness calculated according to eq.1 and eq.2 are smaller than those measured experimentally because of pad influence. The different slope of the curves at higher loading is connected with the different elastic resistance of steel and PE foil. Moreover, substrate influences on MHT results is observed at lower loading than on MHV because the area of elastic deformed material under the penetrating indenter is mach larger than the zone of plastic deformation. So the elastic zone first touches the substrate.

Fig. 3 illustrates MHT profiles for the couple 100μm thick PE foil/steel. In this case the experimental data coincide with calculated ones, i.e. there is not any influence of the substrate.

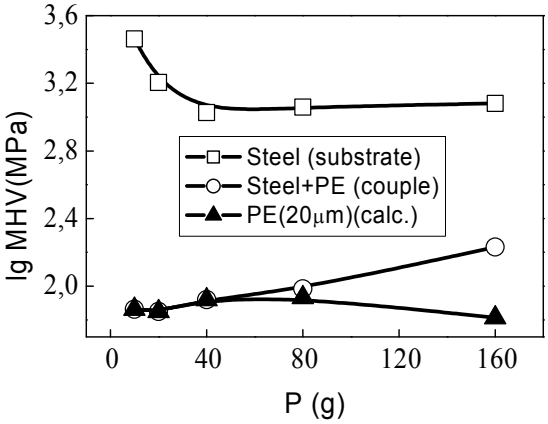


Figure1 Logarithmic dependence of Vickers microhardnes versus applied load for 20μm thick PE foils on the steel

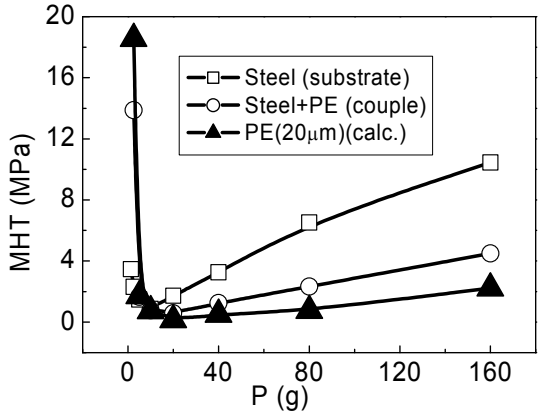


Figure 2 MHT profiles for 20μm thick PE foils on the steel

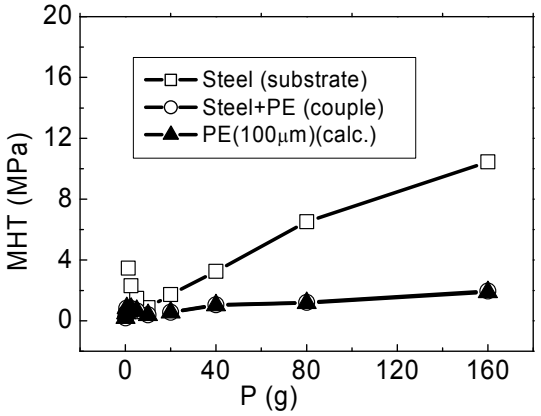


Figure 3 MHT profiles for 100μm thick PE foils on the steel

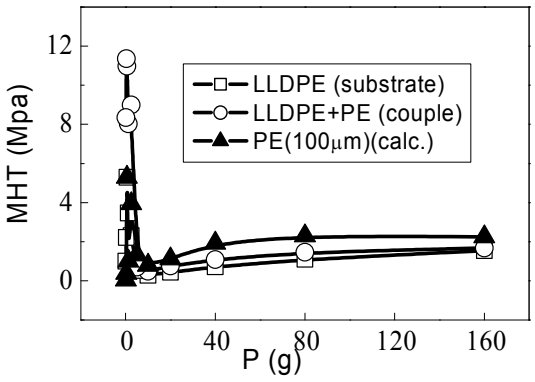


Figure 4 MHT profiles for 100μm thick PE foils on the LLDPE

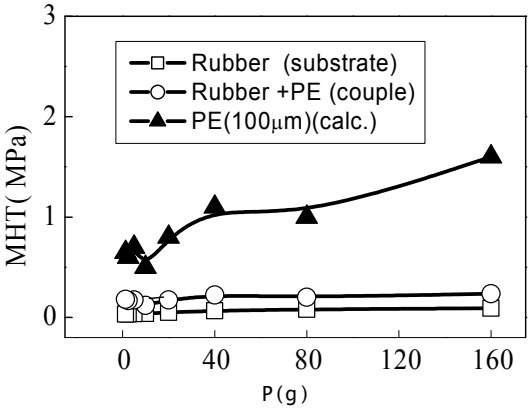


Figure 5 MHT profiles for 100μm thick PE foils on the rubber

In fig. 4 are shown the profiles of total microhardness for couple 100μm thick PE/LLDPE. This is a case when the substrate and the thin material have hardness of the same order. In fig .5 are the same dependencies for 100μm thick PE and rubber as a substrate. The rubber has very small hardness and during penetration the harder PE foils only transfers the indenter pressure to softer substrate. Therefore experimental results are mach closer to that of the substrate than to those of the foil. Fig. 6 present a comparison of the calculated MHT values for the same PE foil (100μm thick) measured on different substrates. The very good coincidence demonstrates the reliability of this method for microharness investigations of thin materials.

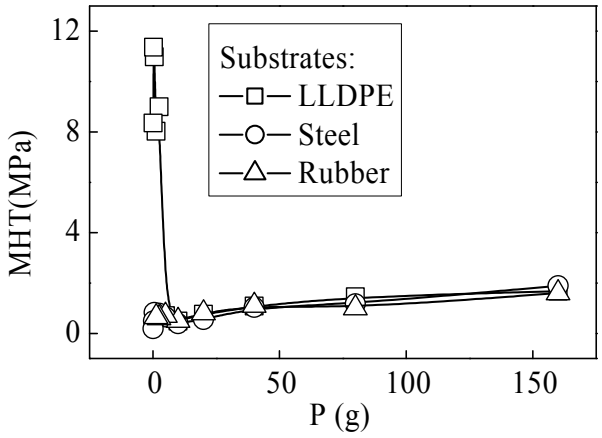


Figure 6 Calculated MHT profiles for 100μm thick PE foils measured on different substrates.

3.4. The graphical method suggested by Oesterle determines the IHV value (Infinitesimales Harte Verhaltens –Infinitesimal Hardness Behaviour). Essentially, this method consist of plotting the regression curve h=f(P) and then interpolating this dependence to the beginning of the co-ordinates, because when there is no load, there is also no indentation. The co-ordinates of a certain point are determined from the interpolated part of the curve. Then the dependence P/h= f(P) is plotted taking into account the experimental points as well as the points from the interpolated zone. The curve is extrapolated up to crossing the ordinate at the so called IHV value. (IHV=limP/h at $P\rightarrow 0$) Fig. 7 illustrates this approach on PE samples. (Ivanov, Zamfirova 1995)

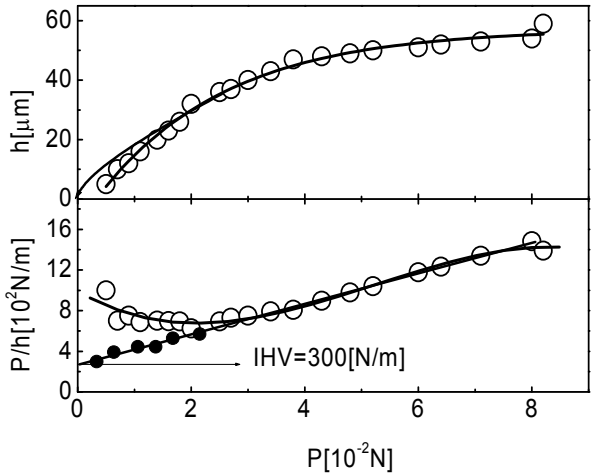
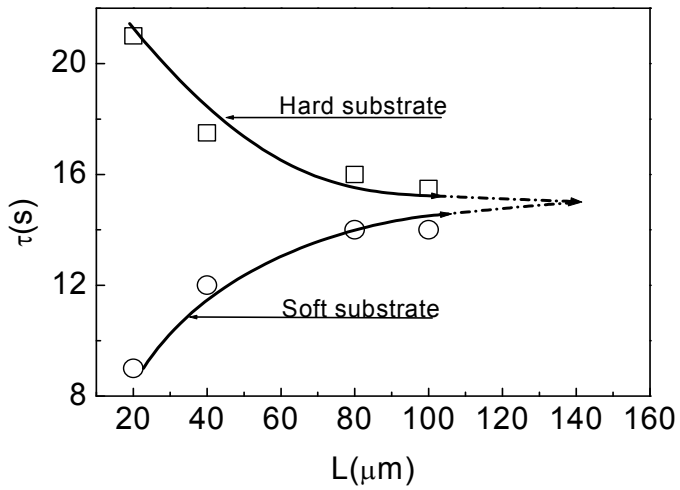


Figure 7 IHV determination of PE foil

3.5. Relative hardness measured by a free pendulum.

The pendulum hardness tester works on the principle of the damping time of a pendulum oscillating on the sample. The device was construed for metal coatings and consists of two hard metal cones with a 60^0 angle at the top. The cones are connected with pendulum. At working position the cones touch the material and are loaded with 60g. The velocity of the pendulum damping is measured. Usually the time (τ) during the initially amplitude reduces by half is determined. This time is proportional to sample hardness because the amplitude of the oscillation reduces faster when the sample is soft. The dependences $\tau = f(L)$, where L is the thickness of the sample are shown in fig. 8. Two measurements have been carried out changing the substrate: hard material- brass and softer material - glossy cardboard. (Tonkov et al., 1992)



Fugure 8 Damping time as a function of sample thickness on different substrates

These two dependencies illustrate the decreasing influence of the substrate with the increasing foil thickness. Extrapolating the two curves to their join is possible tentative estimation of the foil thickness when there is not influence of the substrate. In the case of PE foils and loading of 60g the limiting thickness (L_{min}) is about 140μm. Using a smaller load the limited thickness would be smaller. For hard material as a metals the $L_{min} \approx$ 10μm.

This method is fast and suitable for determination the limits of reliability as well as for comparative measurements. Unfortunately the data obtained by this method could not be used independently because there is not a real numerical expression of this type of hardness.

3.6. The Sclerometric Method allows to evaluate resistance to scratching. It consists of measuring microscopically the width of a scratch made by a diamond under a fixed load, and drawn across the face of the specimen under fixed conditions. This method is used predomonately in mineralogy.

3.7. Nanoindentation uses small loads and tip sizes, so the indentation area dimentiones may only be in the range of a nanometres. Usually a Berkovich tip, which has a three-sided pyramid geometry is employed. Similarly as MHT measurement, a record of the depth of penetration is made, and then the area of the indent is determined using the known geometry of the indentater. This method is very suitable for investigating thin materials but is limited to isotropic materials.

4. Conclusions

MHV and MHT measurements at one and the same applied load are not reliable for characterising the mechanical properties of thin materials because substrate influence at bigger loads and scale factor or imperfectability of pyramid top at lower load could distort the results.

Graphical method suggested by Oesterle is convenient only for materials with significant reversible component of deformation.

Measurements by a free pendulum are a relative and comparative method that requires previous determination of the limiting thickness of the samples for certain applied load.

Our investigations have shown that the method that could provide most correct data is obtaining microhardness profiles by the method of Buckle. It is applicable as for MHV as well as for MHT determination, so it could be used for plastic, elastic and plastic-elastic materials

5. Acknowledgement

This study has been supported by the NSF- Bulgaria, (D002-138/2008-2011) and by the GAAV CR (grant No IAA 200710801).

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