INDENTION MEASUREMENTS AS AN ADEQUATE TOOL FOR MECHANICAL AND STRUCTURAL INVESTIGATION OF NANOCOMPOSITES

Assoc. Prof. Galina Zamfirova PhD., Assistant Prof. M.Sc. Valentin Gaydarov
Transport University “T. Kableshkov”, Geo Milev str. 158, 1574 Sofia, Bulgaria

Abstract: Indentation experiments are a modern investigation method for determination of many mechanical parameters as well as of some structural peculiarities, especially such of polymer composites. In a number of cases they are preferable approach in comparison with classical mechanical measurement because of many advantages: the testing is fast, non-destructive, measuring requires a small quantity of material, those measurements allow establishing structural non-homogeneity and imperfections, etc. By these tests a set of mechanical parameters could be obtained: module of elasticity, creep compliance, yield stress, elastic, plastic and viscoelastic components of the deformation, time dependent characteristics, as relaxation, creep, etc.; especially micro- and nanoindentation which allow investigating at a very small region in the range of um and nm, respectively, could be used for characterizing the structural peculiarities of the samples: degree of crystallinity, lamella thickness, hardness of the composite ingredients, polymorphous changes, etc. So micro- and nanoindentation study could be considered as a link between structural and mechanical parameters. Some of mechanical parameters are widely known, some of them are developed by our scientific group. This report presents examples of applying these methods for characterizing the polymer nanocomposites.

Keywords: MICRO- AND NANOINDENTATION, MECHANICAL PROPERTIES, STRUCTURAL PARAMETERS, NANOCOMPOSITES

1. Introduction

The principle of indentation testing involves touching and indenting the flat surface of the material of interest by another body having a definite characteristic shape and known mechanical characteristic, especially high hardness and elastic modulus. The penetrated body, called indenter, is usually performed by a diamante and according to its geometry measured hardness test can be: Brinel, Knoop, Rockwell, Vickers etc. Hardness measurements can be divided into three groups (macro- micro- and nano-) according to the applied load and consequently to the dimensions of the obtained imprints.

-Macrohardness (H) is used for routine measurements and usually is applied for qualitative control.

-Microhardness is used for studying the relation between mechanical properties and material structure. As microhardness characteristics are sensitive to mechanical properties as well as to polymer morphology, they should be considered as a bridge between the micro- and macro- characteristics of the material. They depend on the applied load (1-200g), on the dimension of the indentation, respectively.

-Nanohardness (NH) enables precise control over the applied load (in nN) and over the indentation depth. This method is used for surface structure studies.

Advantages of these material testing methods are being simple, fast, non-destructive, requiring a small quantity of material for measuring and allowing establishing structural nonhomogeneity, imperfections, macro-, micro and nano-defects.

Taking into consideration the rapid development of the microindentation experiment and wider applications as a scientific method our group contributed to this development inventing some new microindentation methods.

2. Experimental

Basic concepts of this field:

There are two principal approaches to microindentation measurement:

2.1. Classical, conventional indentation tests based on direct measurements of the residual impression left in the sample surface after the removal of load.

1. When use Vickers indenter (a square pyramid with opposite faces at an angle of 136°) Vickers microhardness (MHV) could be calculated according to the equation:

   \[
   \text{MHV} = \frac{P}{d^2} \quad (1)
   \]

   where (P) is the applied load, (d) is the projected diagonal length of the imprint after the indenter realising and (k) is a constant dependent on the geometry of the pyramid. MHV characterises the local plastic material resistance against the penetration and is connected with the irreversible component of deformation, thus characterizes plastic properties of the sample.

   Vickers microhardness correlates with many macromechanical characteristics: module of elasticity (E) \((\text{MHV}=E^2\) [1-4]; yield stress (\(\sigma\)) \((\text{MHV} \approx 3\sigma - \text{Tabor relation}) [5]; sharpness of the maximum in the stress-strain dependencies at neck formation; anisotropy. There is an established similarity between temperature dependencies of the (MHV) and relaxation spectra, DSC measurements, etc. [6].

   On the other hand, (MHV) is sensitive to the some structural and morphological characteristics of polymers: degree of crystallinity, lamella thickness and perfection, hardness of the crystalline phase, polymorphous changes, micro cavities, Curie transition, etc.

   In some cases microhardness could obey the additive law: \(\text{MHV} = \text{MHV}_{x_1} + \text{MHV}_{x_2} + \text{MHV}_{x_1} + \ldots + \text{MHV}_{x_n} \) \(n\) \(\times\) \(x_{\text{MHV}}\) and \(x_{\text{MHV}}\) are the microhardness and mass fraction, respectively, of each component and/or phase. This law can be applied to polymer blends, polymer composites or multiphase systems, as semicrystalline polymers or for studying polymorphous changes.

   2. Determination of Mayer’s lines which are a logarithmic dependence between applied load \((P)\) and dimension of indentation diagonals \((d)\) \([1]\). This dependence comes from Mayer’s power law:

   \[
   P = a\cdot d^n \quad (3)
   \]

   (Respectively in the logarithmic form: \(\log P = \log a + n \log d\), where \((a)\) and \((n)\) are physical parameters. Constant \((a)\) depends on the strength properties and constant \((n)\) depends on the plastic features of the investigated material. The slope of these lines \((n)\) is sensitive to non-uniformity of the structure in the depth of the sample. When \(n < 2\) or \(n > 2\), that means microhardness decreases or increases, respectively, in the depth of the sample. If \(n = 2\) Vickers microhardness is approximately constant along the depth.

   2.2. The microindentation tests developed by our scientific group:

   1. Approximate determination of the mechanical properties according the indentation shape which gives rough information about the elastic-plastic properties of the material investigated. Fig. 1 illustrates schematically some typical indentations observed on the sample surface after removing the indenter: plastic materials \((a)\), elastic materials \((\text{Sinking-in effect})\) \((b)\), materials with prevalent plastic deformation but without contraction \((\text{Piling-up effect})\) \((c)\), fragile materials \((d)\).
2. Determination of total microhardness (MHT) that can be considered as a measure for the local total material resistance against penetration and is related to the total deformation, including elastic, plastic and viscoelastic components. In many investigations the dimensions of the indentation diagonals at loaded state (D) and the microhardness calculated from the so called total microhardness (MHT) is more important for the mechanical and structural study [7, 8]. This parameter is more important, because it gives rather different information about the material structure and mechanical properties and is defined by the analogy of Vickers microhardness:

\[ \text{MHT} = \frac{K_P}{D^2} \] (4)

It includes also the behaviour of the amorphous phase and together with MHV gives information about the elasticity of the material.

2. Determination of microhardness profiles which are sensitive to non-uniformity of the structure in the depth of the sample [9, 10]. Microhardness profiles are dependences of Vickers microhardness or Total microhardness on the applied load (P), respectively, on the penetration depth (h):

\[ \text{MHV} = f(P); \quad \text{MHV} = f(h); \quad \text{MHT} = f(P); \quad \text{MHT} = f(h). \] (5)

Noteworthy is that if in the depth (h) (MHV) and (MHT) respectively, are determined, the value does not correspond to the real microhardness exactly in this depth. This value includes microhardness properties of all the layers situated between the surface and this depth. This method is suitable for characterization of laminated materials and coatings or for tracing changes in the surface layer structure and properties upon chemical, physical or biological treatment.

3. Determination of penetration curves which present dependences of the penetration depth changes (\(\Delta h\)) as a function of time (\(\tau\)) [7, 8, 11]:

\[ \Delta h = f(\tau), \quad (P = \text{const}) \] (6)

This experiment is similar to the creep experiment as a trend of the curves as well as a physical meaning. In both measurements the material is simultaneously subjected to tension and pressure. The difference is that at constantly applied load in the case of penetration the cross section increases during the experiment, while in the case of the creep cross section decreases.

4. Imprint relaxation gives information about the viscoelastic component of deformation. This method is important for studying of materials when load/time dependencies on the deformation are strongly pronounced [12, 13].

2.3. Indentation methods based on the measurement of load–displacement curves at constant loading speed.

The methods is known as a depth-sensing indentation (DSI) or instrumented indentation testing (IIT). Typical trend of the load/unload–displacement curves is shown in Fig. 2. The loading part of indentation cycle may consist of an initial elastic contact, followed by plastic flow, or yield, within the specimen at higher loads. For viscoelastic materials the relationship between load and depth of penetration is not linearly dependent. That is for a given load the resulting depth of penetration may depend upon the rate of load application as well as on the magnitude of the load itself.

Fig. 2 Load/unload–displacement curve

The following microhardness characteristics could be measured using the relationship between the test force and indentation depth measured by a load-unloading test (ISO 14577-1):

- Dynamic hardness (DH) [14]:
  \[ \text{DH} = \frac{a}{F \cdot h^2}, \] (7)
  where (\(F\)) is the value of the instant load at loading and unloading testing regime, \(a = 3,8584\) is a constant which depends on the shape of the indenter and (h) is a indentation depth. This characteristic reveals how the material responds to plastic, elastic and viscoelastic deformation during the test.
- Martens hardness (HMs) [14] was determined from the increase of force/indentation depth curve in the 50% ÷ 90% P interval and characterise the material resistance against the penetration:
  \[ \text{HMs} = 1/(26,43 \cdot m^2) \] (8)
  This characteristic has similar physical sense as dynamic hardness, but characterises the material properties at the maximum indentation depth at constant load.
- Indentation hardness (Hit) [15] according to the model of Oliver-Pharr [1] is a measure for the resistance to permanent deformation.
  \[ \text{Hit} = \frac{P}{24,50h^2}, \] (9)
  where (h) is the depth of contact of the indenter with the test piece.
- Indentation Elastic Modulus (Eit) calculated from unloading part of the dependence by using the equation:
  \[ \frac{1}{E_{it}} \frac{P}{h^2} = \left(1-\nu_s^2\right)E_s + \left(1-\nu_i^2\right)E_i, \] (10)
  where (Ei) is the experimental converted elastic modulus based on indentation contact, (\(\nu_s\)) and (\(\nu_i\)) are the Young's modulus and Poisson's ratio for indenter, respectively.
- Indentation creep (Cit) which is a relative change in the indentation depth at constant test force:
  \[ \text{Cit} = (h_1-h_2)/h_1, \] (11)
  where (h1) and (h2) are indentation depths at the beginning and the final of the creep measurement.
- Plastic and elastic part of indentation work (\(\eta\)) determined from the areas under loaded and unloaded part of the load unload test (\(W = \int \text{Pdh}\))
  \[ \eta = W_{el} + W_{pl} \] (12)

3. Results and discussion

Three examples of microindentation measurement will be given for illustrating their applicability for material characterization: two on nanocomposites and one on polymer films.

3.1. Microhardness investigations on PP/carbon nanotubes nanocomposites applying the classical indentation methods as well as those developed by our scientific team.

Experimental:
Measurement was provided on the standard Vickers microhardness device mhp-160 attached to a microscope UN-2. The investigated materials ware nanocompositions of isotactic
polypropylene (iPP) filled with multiwalled carbon nanotubes (MWCNTs). The outside diameter of the tube was from 10 to 15 nm, the lengths between 1 and 10 μm. The concentration of the filler was studied in the range of 0.05 to 3 wt%. The compositions were calendered as sheets of about 1.5 mm thick and samples with dimensions of 10 x 10 mm were cut for microhardness measurements. All measurements were performed at room temperature. Vickers microhardness and total microhardness were measured for PP homopolymers and for all blends under an applied load of 20, 40, and 80 g. At least ten imprints were made for every point of the figures. Microhardness values were determined within ΔH/H = 0.05.

3.2. Microindentation investigations on epoxy/carbon nanotubes nanocomposites

This example illustrates how microindentation measurements are sensitive to dispersion level and enables distinguishing the good and bad dispersion of the nanoparticles.

Experimental:

Epoxy/carbon nanotubes composites were prepared at OLEM (IMech-BAS) by two different processing modes: with functionalization and without functionalization of the filler. First, (Fig. 4a) carbon nanotubes were functionalized by amine groups by mixing directly in an amine hardener – polyethylene polyamine (PEPA), using high speed mechanical stirring and intensive ultrasonication.  Second, (Fig. 4b) MWCNT were not functionalized with amine, as premixed directly in the epoxy. Further on, the appropriate amount of epoxy/amine was added to the dispersions with subsequent curing for preparation of epoxy/MWCNT nanocomposites.

Fig. 4 demonstrates the concentration dependences of some microhardness characteristics obtained by instrumented indentation testing. (HMs) and (DV) represent the general material resistance against local penetration so as a physical nature are similar to total microhardness measured by a method we have developed. These curves lie under (Hit) curve which represents resistance against irreversible deformation and as a physical meaning should correspond as a trend to Vickers microhardness. From this value Vickers microhardness could be determined using an appropriate correlation coefficient.

The samples prepared by the two modes have different microindentation behavior. The samples without preliminarily functionalized nanoparticles show a decrease of the microhardness parameters at small MWCNTs content (Fig. 4b), which is the usual behavior of common polymer composites. Therefore in this case the nanofiller is not dispersed to nanosizes. The samples with functionalized nanoparticles exhibit an increase in all measured microhardness characteristics at a very small filler content (about 0.03 wt%) due to their better exfoliation (Fig. 4b). However, an additional portion of MWCNTs causes again a diminishing of their hardness values.

Fig. 3 Vickers microhardness (a) and total microhardness (b) vs. MWCNTs content

<table>
<thead>
<tr>
<th>Carbon nanotubes content [%]</th>
<th>Microhardness [MPa]</th>
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<tbody>
<tr>
<td>0.00</td>
<td>100</td>
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<tr>
<td>0.05</td>
<td>110</td>
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<td>0.10</td>
<td>120</td>
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<td>0.15</td>
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<td>0.20</td>
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<td>0.25</td>
<td>150</td>
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<td>0.30</td>
<td>160</td>
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Fig. 4 Some hardness characteristics for samples with functionalization (a) and without functionalization (b) of the filler vs. carbon nanotubes content

<table>
<thead>
<tr>
<th>Carbon nanotubes content [%]</th>
<th>Microhardness [MPa]</th>
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<tbody>
<tr>
<td>0.00</td>
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3.3. Microhardness investigations of foil materials

The microindentation testing is one of the most popular and is almost unique method for determination of mechanical properties of thin films or coatings. Usually the properties of the film are measured combined with substrate giving information of the system as a whole. Then by measuring the properties of the substrate and using some simple calculations is possible to determine the film’s own film microhardness. One of these calculative methods is proposed by Buckle

\[ H'_m = \alpha H + (1 - \alpha) H_s \]  

(13)

where \((H_m)\) is the hardness of the entire system, \((H_s)\) and \((H_f)\) are hardness of the substrate and of the film respectively. \((\alpha)\) is a coefficient dependent on the film thickness, \((L)\), the depth of indentation, \((h)\), and the dimension of the transition region, \((\Delta L)\), (also depending on the surface state, i.e. smoothness and elasticity of the films).

\[ \alpha = \left[1 - \exp\left(h - L - \Delta L\right)\right] \]  

(14)

Fig. 5 plots (MHT) profiles for a steel substrate, compositions steel/PE as well as the calculated curves for PE foil. Two types PE foils with thickness 20 µm (a) and 100 µm (b) were measured.

![Graph A](image1)

**Fig. 5** MHT vs. load P for a steel substrate (black square), compositions steel/PE (red circle), and the calculated curves for PE foil (green triangle). PE foils were with thickness 20 µm (a) and 100 µm (b).

This approach is also applicable for very thin films. However, IIT measurements give larger possibilities. For example, a comparison of load displacement curves between coated and uncoated substrates reveals the difference in the response of the system due to modification in surface treatment. Besides indentation modulus and the different hardness characteristics listed at the beginning of the article, the IIT approach can gives additional information. For instance, the discontinuities in the load-displacement response could show some peculiarities concerning cracking, delamination, plasticity and elasticity of the films.

4. Conclusions:

Summarizing the results it could be said that hardness and elastic modulus are the most measured properties by indentation methods. Both could be measured at different load, indentation depth, respectively, providing a depth profile of these characteristics. Hardness is important because it is related to strength or fracture toughness, elastic modulus could be used for determining the stiffness or compliance of the specimen. The ratio of modulus and hardness \((E/H)\) also provide valuable information about a material since they determine the spatial extend of the elastic deformation that occurs under loading before permanent yielding occurs.

Additional interesting information that these tests may provide is strain hardening, cracking, phase transformation, fracture toughness, energy absorption, anisotropy, manifestation of scale factor and some time dependent mechanical characteristic as a creep and relaxation.

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References: