Microindentation characterization of polymers and polymer based nanocomposites

V. Lorenzo
• Hardness and hardness measurement
  – Vickers hardness
  – Relationships between hardness and other mechanical properties of polymers
  – DSI
  – Microindentation and viscoelasticity
• Microhardness of heterogeneous polymer systems
  – Microhardness of semycrystalline polymers
  – Microhardness of blends
  – Microhardness and physical ageing
  – Microhardness of PMC's
  – Microhardness of PMnC's
• DEFINITION: a measure of the resistance to permanent surface deformation or damage.
  – Local character of measurement
  – What is the meaning of surface damage?

• METHODS OF TESTING:
  – Scratching
  – Static indentation
  – Dynamic indentation
  – ...

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• Static penetration test

• Diamond square based pyramidal indentor (angle between the faces: 136º)
  – Diamond: indentor remains undeformed during the test
  – Pyramidal: geometric similarity of indentations ⇒ hardness is load independent
  – 136º: HV ≈ HB if HB < 600
Stages of the test
Stages of the test
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- Indentor
- Residual indentation

Unloading

Specimen
Vickers hardness definition

- Average pressure on the lateral surface of the residual indentation
- HYP.: the geometries of indentor and indentation are similar \( \Rightarrow \)
  - \( h = \frac{d}{7} \) and \( S_{\text{lat}} = \frac{d^2}{(2 \cdot \sin 68^\circ)} \)
    
    \( d \): diagonal of the base of the residual imprint
    
    \( h \): indentation depth; \( S_{\text{lat}} \): contact area
  
- \( HV = 2 \cdot \sin 68^\circ P/d^2 \)
  
  \( HV \): Vickers hardness; \( P \): load

- MICROHARDNESS: hardness measured after applying small loads (grams) \( \Rightarrow \) diagonal of the residual indentation: \( \mu m \)
Microindentation of polymers

Stress distribution under the indentor

- Classical results and FEM calculations:
  - Stresses are confined to a hemispherical region with radius \( \approx 1.5d \approx 10h \)

- Some practical considerations:
  - Minimal distance between two indentations
  - Minimal distance between indentations and edges
  - Minimal thickness of films
  - Very small sample quantity (ng)
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**Relationships between MH and other mechanical properties**

![Graph showing relationships between MH and other mechanical properties](image)
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**DSI: Depth Sensing Indentation**

- 1980's: continuous measurements of load and indentation depth
- Very small loads (mN) ⇒ resolution: µN
- Very small indentation depths (tenths of µm) ⇒ resolution: nm
- Berkovich indenter

Results of DSI tests

- Hardness under load
- Creep
- Elastic modulus
- Delayed elastic recovery
- Deformation energy
- Recoverable energy
- ...
- And, of course, hardness
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100 \frac{h(t)}{d} = \alpha + \beta \exp\left(-\frac{t}{\tau}\right)

Delayed elastic recovery study by means of DSI measurements

V. Lorenzo et al.: communication to EPF2011, Granada, 26th June-1st July
Creep study by means of DSI measurements

- Model:

\[ h^2(t) = \frac{\pi}{2} P_0 \cotg \alpha \left[ \frac{1}{E_1} + \frac{1}{E_2} \left( 1 - \exp \left( \frac{E_2 t}{\eta_2} \right) \right) + \frac{t}{\eta_1} \right] \]

### Table

<table>
<thead>
<tr>
<th>Sample</th>
<th>E (MPa)</th>
<th>( \tau ) (s)</th>
<th>Cit (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>410</td>
<td>0.48</td>
<td>23</td>
</tr>
<tr>
<td>S</td>
<td>675</td>
<td>0.46</td>
<td>18</td>
</tr>
</tbody>
</table>

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Delayed elastic recovery study by means of DSI measurements

Model:

\[ h(t) = h(0) + A(1 - \exp(-t/\tau)) \]

- Retardation time, \( \tau \), structure independent
- Not a quantitative agreement
  - Interferometry experiments
    - Indenter geometry
    - Sampling frequency
  - Creep results:
    - Non linearity

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Local character of the measurement

- Microindentation “averages” the properties of some $\mu m^3$ of the material around the indentor.

- Microindentation and heterogeneity of the specimen:
  - Characteristic length of heterogeneities $> d \Rightarrow MH = f(x, y)$
    - Information about distribution of phases
    - Characterization of phases
  - Characteristic length of heterogeneities $< d \Rightarrow MH$ is not a function of the position
    - Bulk properties of the material
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Polyethylenes that has been quickly cooled form the melt:

- Length of crystallites < d ⇒ MH is not a function of the position ⇒ MH is an increasing function of crystallinity level
- Information about deformation mechanism

• It is not possible to obtain a 100% crystalline or amorphous PE sample.

• Mechanical properties of phases can be obtained by extrapolating MH measurements


• Isothermally crystallized iPP displays spherulites of the α and β polymorphs ⇒ properties of the α and β spherulites

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Blends of miscible A and B polymers: homogeneous at d scale \( \Rightarrow \)
\[ MH = f(\%A) \]

Blends of inmiscible A and B polymers: separated domains of A and B

- If \( \%A < \%B \Rightarrow \) characteristic length of A domains < d \( \Rightarrow \) MH is a continuous function of \( \%A \)
  - Continuity of MH(\( \%A \)) \( \Leftrightarrow \) miscibility
- If \( \%A \) is comparable con \( \%B \):
  - Characteristic length of A domains \(< d\)
  - Characteristic length of A domains \(> d\)
    - MH is a function of the position
    - Characterization of individual phases
Microhardness of blends of PEO with iPMMA

Microhardness of blends of polyolefins and LCP's

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Microhardness and physical ageing

- A – Tg: liquid
  - Cooperative movement of chains
- Tg – B: glass
  - Movements of local groups
- B – C: physical ageing
  - Densification:
    - Local free volume fluctuations
    - Correlation length $< 10^{-1} \, \mu m$
Physical ageing of LCP's and SMP's as revealed by MH tests


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Composites are multiphasic materials: fillers dimensions ~ some tens of µm ⇒ characteristic dimensions of heterogeneities > d ⇒ MH is position function ⇒ MH is not an adequate tool for characterizing composite materials

But it can be used for:

- Characterizing matrix and fillers.
- Characterizing interphases:
  - Transcrystalline structures in GF reinforced PP composites
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• Agglomerated fillers:
  – characteristic length of heterogeneities > d ⇒ MH is a function of position
• If the fillers are well dispersed:
  – characteristic length of heterogeneities < d ⇒ MH = f(% filler)
  ⇒ information about the reinforcement effect of the filler.
PC-clay nanocomposites obtained by dissolution

Microindentation of polymers

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Other heterogeneous polymeric materials

- Characterization of coatings
- Multi-layer extrusion
- Skin-core structures in injection molded polymers
- Composition gradients
- ...
• Microindentation is an adequate tool for exploring structure of polymeric materials.

• The volume of material that is deformed in hardness test is around $d^3$.

• The information that can be obtained from a hardness test depends on the characteristic length of the heterogeneities of the sample, $l$:
  - If $l < d$, bulk properties of the material.
  - If $l > d$, local character information.
The research group

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  – Prof. V. Lorenzo

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Thank you very much for your attention

Merci pour votre attention

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