

Challenges and Progress in High-Throughput Screening of Polymer Mechanical Properties by Indentation

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Depth-sensing or instrumented indentation is an experimental characterization approach well-suited for high-throughput investigation of mechanical properties of polymeric materials. This is due to both the precision of force and displacement, and to the small material volumes required for quantitative analysis. Recently, considerable progress in the throughput (number of distinct material samples analyzed per unit time) of indentation experiments has been achieved, particularly for studies of elastic properties. Future challenges include improving the agreement between various macroscopic properties (elastic modulus, creep compliance, loss tangent, onset of nonlinear elasticity, energy dissipation, etc.) and their counterpart properties obtained by indentation. Sample preparation constitutes a major factor for both the accuracy of the results and the speed and efficiency of experimental throughput. It is important to appreciate how this processing step may influence the mechanical properties, in particular the onset of nonlinear elastic or plastic deformation, and how the processing may affect the agreement between the indentation results and their macroscopic analogues.

1. Introduction

For several reasons related to high signal precision and low material volumes probed, depth-sensing indentation (DSI) is the preferred technique for studying the mechanical properties of polymeric materials. Other names for this technique include “instrumented indentation” and “load and depth-sensing indentation”. The latter name is a very accurate description of how the technique actually works: the load applied on a rigid probe and the displacement of that probe into the surface of the

material under investigation are measured simultaneously.^[1,2] From the load and displacement recorded at each time-step during the indentation experiment, and knowledge of the indenter probe geometry and mechanical properties, the mechanical properties of the material of interest can be evaluated. The imposed strains and stresses in the material depend, among other factors, on the probe geometry and the constitutive mechanical behavior of the sample material. The indentation depths employed during indentation experiments range from several nanometers^[3] to the millimeter range.^[4] If the indentation response is to be representative of the bulk form of the material, it is important that the maximum indentation depth is sufficient to probe a representative material volume.^[5] Related to the indentation depth, alternative names for the technique are microindentation,^[6] ultra-microindentation,^[7] and nanoindentation.^[2,8] Strictly speaking, nanoindentation refers to DSI for which the maximum load or maximum depth is less than 100 nN or 100 nm, respectively.

DSI is a very suitable technique in the field of thin-film or coating technology. Mechanical properties of thin polymeric or hybrid films deposited on a substrate, as well as mechanical property gradients within the film, can be investigated by indenting either on the surface of the film or along cross sections of the film.^[9,10] DSI is the preferred technique if the amount of material available for testing is limited, owing to either limited material supply or prohibitive material cost. Such limited

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availability of material may arise during classical chemical synthesis of new materials on a small scale^[11] or during rapid analysis of new property correlations by means of combinatorial or high-throughput experiments.^[12–15]

This Report charts the progress in high-throughput experimentation (HTE) as applied to polymer mechanical properties obtained by DSI. Progress in throughput of the HTE screening as well as in classification and interpretation of the HTE output data is discussed. From the high-throughput experiment, an increasing number of material properties can be obtained in principle. We briefly assess the progress in correlation between various macroscopic properties and their counterparts obtained by means of indentation. In order to understand both the challenges in the quest for a better agreement between indentation results and macroscopic properties, and the effect of HTE sample preparation on the indentation results, the molecular origin of the mechanical properties of glassy polymers is briefly discussed.

2. Molecular Origin of Mechanical Properties of Polymers and Comparison Between Macroscopic and Indentation Results

2.1. Elastic Modulus

The modulus of elasticity of materials under uniaxial tension, also called E-modulus or Young's modulus, describes the material stiffness at small strains or the resistance of the material to reversible deformation. The Young's elastic modulus E is defined as the initial slope of a stress–strain diagram obtained during a uniaxial tensile test. Polymers are viscoelastic, meaning that the elastic properties depend on the time of observation and time of loading, but the initial or rapid response of polymers is often still characterized by an elastic modulus. The Young's elastic modulus of glassy polymers is governed principally by interchain interactions.^[16] Usually, the relatively weak van der Waals interaction is the most important interchain interaction, and the resulting E of glassy polymers typically ranges from 2.5 to 4.5 GPa.^[17] Extensive thermal annealing may result in local rearrangement of small parts of the macromolecule and therefore in a slight increase of the interchain interactions and thus in the modulus of the elasticity.^[18] However, such changes are usually not so large that the thermal history information is included in databases presenting E of glassy polymers.^[19,20]

The relations between contact load and displacement for flat-punch, spherical, or conical indenters into a linear-elastic solid were derived by Boussinesq,^[21] Hertz,^[22] and Sneddon.^[23] For a flat punch, a sphere (with a radius much larger than the indentation depth), and a cone (or Berkovich tip, which is a pyramid with a triangle as a base and a center-to-face angle of 65.3°^[24]), the force and the displacement are related by a simple power-law relation with the prefactor depending on the Young's elastic modulus and the geometry, and the power depending on (again) the indenter geometry.^[24] Therefore, for linear-elastic materials not showing any plasticity, E can be evaluated when the load and displacement are measured and the indenter geometry is known.



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Based on load–displacement relationships derived by Sneddon, Oliver and Pharr developed an analysis method to obtain the Young's elastic modulus from the indentation experiment that is well-suited for elastic-plastic materials.^[1,25,26] This analysis method is widely applied in HTE studies employing DSI^[12,14,15] as it offers facile, HTE-compatible data handling,

and displays the trends in material stiffness within the HTE library. In this analysis, the reduced modulus E_r is calculated from the stiffness at the onset of the unloading S and the projected area of contact between the probe and the material A_c . (The coefficient β is related to the indenter geometry, and is slightly larger than 1^[25]).

$$E_r = \frac{\sqrt{\pi}}{2\beta} \cdot \frac{S}{\sqrt{A_c(h_c)}} \quad (1)$$

The area of contact depends on the contact depth h_c , which is calculated as shown in Figure 1. The initial unloading slope S is obtained by fitting the unloading load–displacement response. The fit function, and the relation of the parameters m and ε to the shape of the indent, are discussed elsewhere.^[2,25,27] As elastic displacements occur both in the specimen (with modulus of elasticity E_{sample} and Poisson's ratio ν_{sample}) and in the indenter, the elastic modulus of the sample is calculated from E_r using

$$E_{\text{sample}} = \left(1 - \nu_{\text{sample}}^2\right) / \left(\frac{1}{E_r} - \frac{1 - \nu_{\text{indenter}}^2}{E_{\text{indenter}}}\right) \quad (2)$$

For polymers, the modulus obtained by the Oliver and Pharr method is significantly higher than the macroscopic Young's elastic modulus: the reported differences range from 70% for polystyrene (PS) and polycarbonate (PC),^[28] to 67% for polymethyl methacrylate (PMMA) and 46% for PC,^[29] to 20% for poly(benzocyclobutene)^[2] (all using a Berkovich indenter). Several factors contribute to the discrepancy between E obtained by the Oliver and Pharr method and the macroscopic Young's elastic modulus.

First, the Oliver and Pharr analysis assumes that the unloading is elastic,^[1] while viscoelasticity applies for polymers. An additional complication is the nonlinearity of the viscoelastic deformation that occurs when polymers are strained to above 1–2%.^[2,30] Experimentally, one observes that when the indent is reloaded directly after the unloading, the reloading does not

coincide with the unloading response, indicating that the unloading is not simply elastic. The slope of the load–displacement response at the end of the reloading is lower than at the onset of the unloading.

Second, the creep influences the obtained S , and thereby E (Eq. 1). Procedures have been proposed to correct S for the creep based on the creep rate prior to the unloading.^[27,31] For polymers, quick unloading is recommended to ensure that the unloading is predominantly elastic.^[32]

Third, in the Oliver and Pharr procedure, also A_c depends on the initial unloading slope S , see Figure 1.^[1] As different unloading rates result in different S , we end up with the situation that A_c (which should depend on what happened prior to the unloading) mathematically depends on the unloading itself. Cheng and Cheng^[32] proposed an approach to calculate h_c , and thus A_c , from the maximum displacement h_{max} only. However, that procedure requires that the (visco)elastic deformation is linear and that no plastic deformation occurs.^[32]

Moreover, around the indent perimeter, material may pile up, resulting in a larger contact area A_c than inferred from the Oliver and Pharr procedure. As a consequence, too low an A_c is used in the calculation and E is overestimated (Eq. 1). Finite element simulations (where the material was modeled as an elastic-plastic material not exhibiting strain softening prior to the strain hardening) showed that the Oliver and Pharr method underestimates the real contact area significantly if the material has a low yield stress compared to the elastic modulus, and has little or no capacity to work-harden.^[33] The amount of pileup also depends on the yield stress and the strain softening (discussed below).^[34] As these material properties may vary throughout the HTE library, the ratio between the real projected contact area and A_c obtained by the Oliver and Pharr method may vary to some extent. In extreme cases, this might even obscure the trends in elastic properties within the HTE library. Therefore, it is advisable to image some of the residual indents by atomic force microscopy (AFM) or by scanning the indenter over the indented surface. Based on the ratio of the final depth to the maximum indentation depth, Tranchida et al.^[28] expected the influence of the pileup on E to be modest for most glassy polymers.

A last factor is that for shallow indents (up to 50 nm) the Young's elastic modulus may differ from that of the bulk owing to confinement effects.^[3] If a material is compressed in one direction, it expands in the orthogonal directions. Impeding that expansion may increase the material's resistance to deformation by up to 35%, 60%, or 114% for a material with a Poisson's ratio of 0.3, 0.35, or 0.4, respectively.^[28] The shallower the indent, the more effective this impediment may be, due to intrinsic length scales of the material such as the polymer chain length.^[3] For HTE experiments, this confinement effect is an undesired complicating factor. In non-HTE studies, however, investigating this effect may provide insight into polymer chain dynamics, which may result in nanostructured materials with improved properties.^[3]

From the loading branch of the load–displacement response obtained with a flat punch indenter (Fig. 2), E can be derived in a way that circumvents some of the problems mentioned above.^[35] The advantages of this probe geometry include that the contact area is constant and independent of the indentation depth, no assumptions on the contact perimeter are required and, initially,

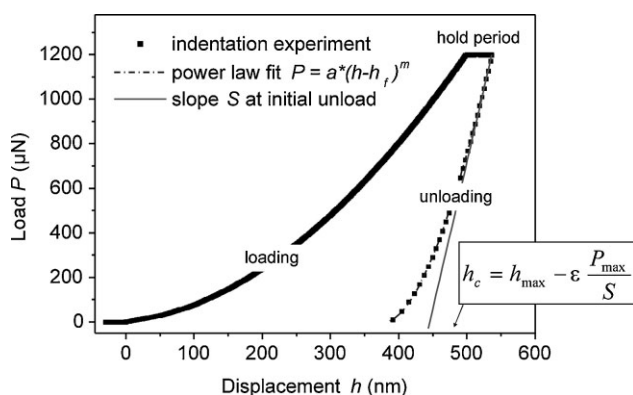


Figure 1. Load–displacement response obtained upon indenting polystyrene with a Berkovich indenter, showing the fit applied in the Oliver and Pharr method to obtain the slope S at the onset of the unloading step as well as the contact depth h_c . P_{max} and h_{max} are the load and indentation depth just prior to unloading, respectively. The final displacement h_f is the (fitted) indentation depth after unloading.

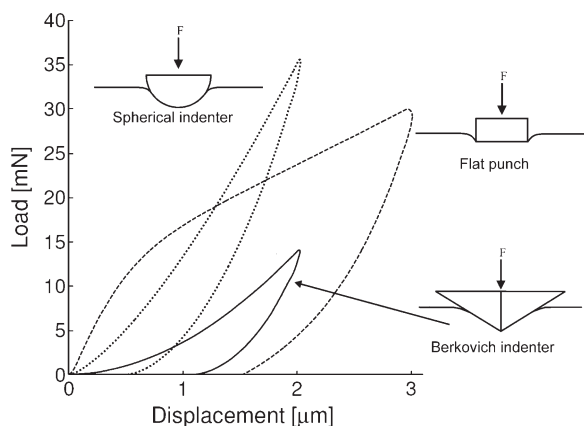


Figure 2. Load–displacement responses for indentation employing various probe geometries on polycarbonate: Berkovich tip (solid line), sphere (dotted line), and flat punch (dashed line). Reproduced with permission from [18]. Copyright 2008 Eindhoven University of Technology.

plasticity is negligible.^[35] Unfortunately, that geometry is very sensitive to tip–sample misalignment: 1° misalignment results in approximately 10% difference in E . It is possible to minimize the misalignment.^[35] However, performing an alignment procedure for all members of the HTE library is time-consuming and is therefore not HTE-compatible.

The Field and Swain method^[36] is another approach to obtain E that has also been used in a HTE context.^[13] Partial-unloading indentation experiments are performed using a spherical indenter with a large radius relative to the indentation depth. The load and displacement before and after partial unloading are analyzed using a modified version of the Hertz equation, assuming elastic or elastic-plastic material behavior. The Field and Swain method is numerically not as sensitive to errors in initial surface detection as the original Hertz analysis.

Other approaches modified the Hertz or Boussinesq analysis to account for the viscous response, and determine both the initial elastic modulus and the material viscosity from the loading response of the material.^[6,29,37,38] This allows the time-dependent polymer properties to be studied.

2.2. Creep and Relaxation Properties

Viscoelasticity (or viscoplasticity) is often probed by applying a constant load and measuring the deformation of the test specimen over a long time period.^[39] A simplified mathematical description of the displacement increase with time can be obtained by the Voigt or Kelvin model, which consists of a spring and a dashpot in parallel.^[16,39] Alternatively, one could impose a sudden uniaxial deformation and measure the stress, which will decrease with time owing to relaxation of the polymer chains. The Maxwell model, consisting of a spring and a dashpot in series, provides a simple description of this stress decrease.^[16,39] Other models exist that describe the creep and relaxation behavior more accurately at the expense of using more parameters.

To determine viscoelastic properties, typically a flat punch^[6,37] or a large-radius spherical indenter^[6,30,38] is used in order to

prevent plasticity and nonlinear elasticity, although also experiments are performed with a Berkovich indenter.^[29,40,41] (The dependence of the strain on the indenter geometry is discussed in Sec. 2.4 on yield stress.) Apart from analytical approaches to discriminate between viscous, elastic, and (visco)plastic deformation,^[32,40,41] numerical approaches have been developed as well.^[18,32,34,42] Another challenge for obtaining viscoelastic and viscoplastic properties from indentation creep or relaxation experiments originates from the (thermal) drift in the experiment, which could become a significant error source during lengthy experiments. Furthermore, for larger tip radius (chosen to avoid nonlinearity and plasticity), the measurement becomes more sensitive to tip–sample adhesion, surface roughness, and surface detection uncertainties.^[24,43]

Good agreement was found between the time-dependent relaxation modulus $G(t)$ and Poisson's ratio ν determined by microindentation (in combination with strain measurements) and by a uniaxial test for PMMA and epoxy,^[6] while less good agreement was observed for experiments performed with “sharper” indents due to nonlinear deformation behavior.^[43]

2.3. Loss Tangent and Storage Modulus

When an oscillating force or displacement is imposed on a material, the imposed mechanical energy is partly dissipated and partly stored. The first response is typical for a fluid, whereas the latter is typical for an elastic solid. The loss tangent indicates the ratio between the two responses.^[16,17,39] Superposing a small oscillation on the quasi-static load or displacement profile (“dynamic DSI”), allows frequency-dependent viscoelastic properties to be extracted.^[24,44] It is noted that in most dynamic indentation analysis protocols the contact depth, and thus the contact area, is calculated from the stiffness (the ratio of the load amplitude to the displacement amplitude) measured during the oscillation.^[24] As this stiffness depends on the frequency, the contact depth mathematically depends on the frequency, which is not physically true.^[45] A comparable issue has already been addressed in Section 2.1 on the elastic modulus. In addition, the dynamic DSI loading conditions differ from those in standard macroscopic rheological techniques.^[46] Nevertheless, the storage modulus derived from dynamic indentation matches its macroscopic counterpart reasonably well, as observed for PMMA and two types of poly(dimethylsiloxane).^[46] In contrast to the storage modulus, the loss tangent obtained by dynamic DSI is not dependent on the contact area and therefore not affected by inaccuracies in the contact depth determination.^[47] Hayes et al.^[47] established a master curve for the loss tangent using dynamic indentation, making use of the time–temperature superposition principle. The glass transitions of poly(cyanurate) and epoxy resin obtained from these master curves were in agreement with the glass transitions found by dynamic mechanical thermal analysis (DMTA) at the same test frequency (Fig. 3).

2.4. Yielding, Strain Softening, and Strain Hardening

Yielding of a glassy polymer can be considered as mechanically passing the glass transition: the polymer segment mobility is

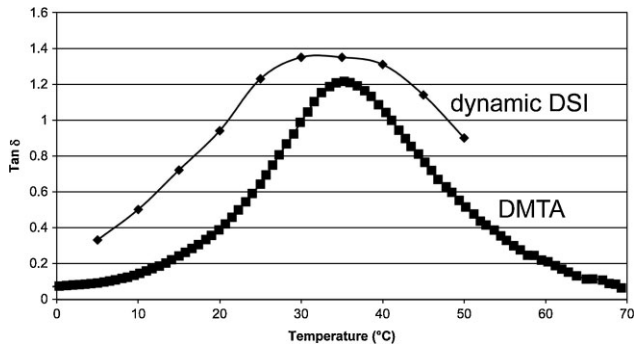


Figure 3. The glass transition temperature of an epoxy resin, as identified by a peak in the loss tangent during DMTA, correlated well with that identified by dynamic DSI on a heated sample. Reproduced with permission from [47]. Copyright 2004 Materials Research Society.

increased owing to the applied mechanical stress.^[48] In analogy to the time–temperature correspondence, which states that at a shorter time scale, that is, a higher test frequency, one finds a higher glass transition temperature T_g ^[17] also a time–load correspondence (a higher strain rate results in a higher yield stress)^[48–50] and a temperature–load correspondence (a higher temperature results in a lower yield stress)^[50,51] exist.

The magnitude of the yield stress depends on the thermal history of the sample (Fig. 4). A long thermal treatment just below the glass transition induces local rearrangement of small parts of the macromolecule, thereby increasing the interchain interactions and thus increasing the yield stress. Compressive testing can be used to study the stress and strain behavior of the material beyond the yield point, as, in contrast to tensile testing, localization of the deformation phenomena is minimized.^[52–54] As the load–displacement response and the contact area development during the indentation experiment depend on the yield stress, the strain softening and the strain hardening,^[18] several findings from uniaxial compression tests combined with modeling are summarized here.

- After yielding, the polymer often shows a stress decrease (strain softening), followed by a stress increase (strain hardening).

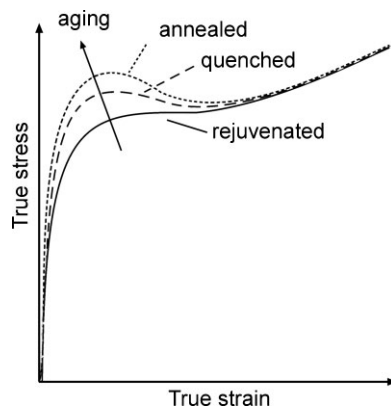


Figure 4. Compressive stress–strain curves for polycarbonate. The yield stress and the amount of strain softening after yielding strongly depend on the thermal history of the sample. Reproduced with permission from [54].

ening). This strain hardening originates from the resistance to deformation of the entanglement network.^[52]

- The yield stress can be quantitatively described as a function of the annealing time and temperature. Mechanical rejuvenation, for instance by cold rolling, erases the thermomechanical history of the material and reduces the yield stress, sometimes even so much that after yielding the material does not strain-soften.^[49]
- For larger plastic strains, the relation between stress and strain does not depend on the thermal history (as long as the thermal history was not so severe that it caused crosslinking or degradation). Therefore, the strain softening guides the stress–strain curve from the yield point to the same strain hardening curve for all thermal histories.
- The strain hardening relates to the entanglement density.^[52,54] A material with a low entanglement density (many repeat units between entanglements, e.g., polystyrene) exhibits less strain hardening than a material with a higher entanglement density (e.g., polycarbonate).

Yielding occurs when the stress and the strain exceed critical values. The strain and the strain gradient in the probed material depend on the indenter geometry. Using the representative strain ϵ_{repr} as a rough descriptor for the characteristic strain, we observe that for conical indenters, the representative strain depends on the cone angle α .^[24]

$$\epsilon_{repr} = \frac{0.2}{\tan \alpha} \quad (3)$$

A sharper cone induces higher strains in the sample material. A Berkovich indenter results in a moderate representative strain level of approximately 8%.^[24] Considering that typical strains at yield for glassy polymers range from 1% to 8%,^[20] plasticity occurs right from the start of the indentation experiment for Berkovich indenters. For spheres (Fig. 2) with radius R , a representative value for the strain is^[24]

$$\epsilon_{repr} = 0.2 \frac{a}{R} \quad (4)$$

where a describes the radius of the circle of the tip–sample contact perimeter. With increasing load, the contact radius and, thus, the contact strain increase. Therefore, plasticity sets in gradually for indentations performed with a sphere. For flat punch indentations, the transition from (visco)elastic to (visco)plastic deformation shows up as a sudden decrease in the slope of the load–displacement response (Fig. 2). With increasing yield stress, this bending of the loading response occurs at higher indentation load and displacement, and the slope of the post-yield branch of the loading curve is increased.^[18]

The yield stress of glassy polymers is not (yet) easily deducible from the indentation data by means of simple equations. By (non-HTE) finite element modeling, Pelletier et al.^[18,34] were able to predict the load–displacement loading responses for flat-punch and spherical indentations on polycarbonates using an elastic–viscoplastic material model and independently determined material parameters, including the yield stress (which was varied

by a thermal treatment). Their model was also able to predict the effect of the loading rate during the indentation experiment. Also the contact area development was determined experimentally as well as by modeling, showing that for spherical indentation a slightly larger contact area was found for shallow indents on the polycarbonate with the lower yield stress because for this material more plastic deformation occurs. For deeper indents, however, the contact area was somewhat larger for the high-yield-stress material, owing to larger strain softening (which causes pileup) for this material.^[34]

2.5. Hardness

The hardness is a measure of the resistance to local deformation of a material. The hardness of the material depends on a combination of the elastic modulus, yield strength, and strain-hardening capacity of the material.^[55] Various hardness measurement methods exist: the Shore hardness, which has been developed for elastomers and soft polymers, is calculated from the penetration depth of a spring-loaded indenter,^[56] while the Rockwell hardness (usually applied for “harder” plastics such as nylon, polycarbonate, and polystyrene) is calculated from the depth of the residual impression.^[55,57] For Shore and Rockwell hardness tests, various scales exist, employing different loads and indenter geometries. The Vickers and Brinell hardnesses are calculated from the lateral dimensions of the residual impression, which are measured by optical microscopy after removing the indenter.^[55] The Vickers geometry is a pyramid with a square as the base plane, while in the Brinell experiment a 10 mm diameter spherical indenter is used.^[55] The Berkovich indenter, which is often used in DSI, has a triangle as the basal plane and opening angles such that its ratio of projected area A_c to depth h_c is the same as for the Vickers probe.^[24] The Berkovich probe is more suited for small-scale indentation, as a three-sided indenter allows better convergence to a point at the tip apex, while a four-sided Vickers probe in practice converges to a (small) line.^[24]

The mean contact pressure at the onset of unloading in the DSI experiment is often taken as a measure of the hardness H of the material. It is calculated from the load at the start of the unloading P_{\max} and the total projected contact area A_c (which is obtained from the contact depth h_c and the indenter shape):

$$H = \frac{P_{\max}}{A(h_c)} \quad (5)$$

For metals, usually a good correlation exists between Brinell^[58] or Vickers^[59,60] hardness and either yield stress or tensile strength, thus presenting the hardness as a measure for plasticity (and not so much for elasticity). The hardness of polymers obtained by DSI, however, does not reflect the resistance to plastic deformation only, but is substantially influenced by the elastic deformation.^[61] The relation between the indentation modulus and hardness of various copolymers, obtained using a self-similar indenter, is provided as Supporting Information. These results show that either the plastic deformation of these materials scales with the elastic deformation or the indentation hardness has significant “cross talk” with the elastic modulus.

The hardness is not a real material property for polymers, as it depends strongly on the loading history.^[45,62] Viscoelasticity influences the measured hardness: elastic deformation that does not recover quickly enough upon unloading results in a higher contact depth h_c and thus a higher contact area A_c , thereby reducing the hardness H (Eq. 5). However, in a relative sense, this metric can be used to compare different polymers.

2.6. Concluding Remarks on Obtaining Mechanical Properties by DSI

Topography information can be obtained by imaging the indented surface using the indenter probe or using an atomic force microscope mounted on the indenter system. Such topography information provides the opportunity to obtain more parameters or better quality parameters from the indentation experiments.^[63] For instance, insight into the surface tilt or the amount of pileup helps to assess the quality of the obtained indentation modulus. The drawback is, of course, that this imaging step greatly reduces the experiment throughput.

Another consideration on indentation on polymers relates to orientation and (semi)crystallinity. The crystallites in semicrystalline polymers are anisotropic: their properties differ for the various crystallographic directions. If the crystallites are small (compared to the length-scale of testing) and distributed — as well as oriented — randomly, the overall material is still isotropic. In this case, the stiffness obtained by DSI still provides a suitable average of the elastic property of the material. However, some processing steps (e.g., extrusion) can introduce orientation. For materials exhibiting orientation, indentation can be combined with post-test imaging to study the degree of orientation. However, some of the standard analysis methods may be inaccurate, as they assume an isotropic mechanical response.

If the indentation experiments are performed under load control conditions, the same load function results in differences in the unloading rate [nm s^{-1}] and in the indentation contact depth between various members of the HTE library investigated. If experimental factors, such as the unloading rate^[64,65] or indentation contact depth,^[8] result in variation of the obtained mechanical properties, this variation should end up in the standard deviation describing the uncertainty in the obtained property for each library member, and not as a difference between library members. This is ascertained when one repeats the experiment at a couple of different maximum loads P_{\max} .

In the case that indentation is used for HTE testing of polymer material properties, it is recommended to indent more than 100 nm into the material, as in this case the response originating from the top 10 nm of the polymer film, which is reported to have a different T_g ^[66] and different mechanical properties,^[3,67] is minimized. An extra advantage of not using very shallow indents is that the initial surface detection (h_0) and the tip apex defect become less critical as well.

3. High-Throughput Experimentation

Excellent reviews on HTE and combinatorial materials research in the field of polymer science have been given by Meier et al.^[68,69]

and, more recently, by Webster.^[70] The latter author describes a combinatorial experiment as one “where a relatively large number of chemically distinct, but related, compositions are prepared and analyzed for their key properties”.^[70] In order to improve the time efficiency, “a combinatorial experiment is usually carried out using high-throughput techniques, which enable the preparation and screening of multiple materials in a single experiment”.^[70] These multiple materials together are called a “library”. Optimal understanding of the structure–property relationships present in the combinatorial library and optimal time efficiency can be realized by implementing the following steps in the combinatorial workflow:^[69]

1. Design of experiment: choosing the experimental variables for the different members of the library such that the experiment maximizes the gained knowledge, while the number of members is kept to a minimum. Advanced methods exist to make use of prior knowledge to optimize the choices for the experimental variables.^[71]
2. Automated (parallel) synthesis and/or formulation.
3. Deposition of the materials as thin films or as dots.
4. High-throughput investigation of those films or dots by spectroscopy, DSI, or other characterization methods.
5. Advanced data handling allowing facile visualization and/or mathematical description of the structure–processing–property relationships present in the dataset.^[72]

After performing these five steps, one may use the obtained knowledge, the questions remaining, and/or the new questions that arose from the combinatorial experiment to design the next combinatorial experiment.^[69] Alternatively, one can “zoom in” to a part of the parameter space that showed interesting “leads” or “hits”, to identify even more optimal results by a finer-meshed investigation of that part of the parameter space.^[73,74] Design of experiment (step 1), advanced data handling (step 5), and proper integration of all steps of the combinatorial workflow significantly improve the information output of the experiment.^[72] During combinatorial experiments, many different materials are made (step 2) but the amount of sample for each material is generally small. Typically, polymer amounts of 100 mg (an example from a polyolefin catalyst optimization study by Bousie et al.^[74]) to 500 mg (sequential robot-assisted cationic ring-opening polymerization by Hoogenboom et al.^[75]) are synthesized. Therefore, HTE techniques should be capable of providing reliable information on the material property of interest while using only small amounts of material.

Krupicka et al.^[9] investigated whether indentation and scratch testing are suitable tools to evaluate the performance of organic coatings. They found that in a limited time reproducible data on indentation modulus, elastic recovery, and scratch depth were generated, and rupture could be identified, together with the load at which the rupture occurred. Such indicators may help in understanding coating performance such as mar resistance. Another evaluation of the suitability of indentation as a HTE screening tool, focusing on elastomers, showed a good correlation between indentation and Shore A hardness.^[76] Tweedie et al.^[12] synthesized, in triplicate, 576 unique polyacrylate compositions by printing 70:30 and 30:70 mixtures (by volume) of 24 different acrylates followed by photopolymerization (combination of steps

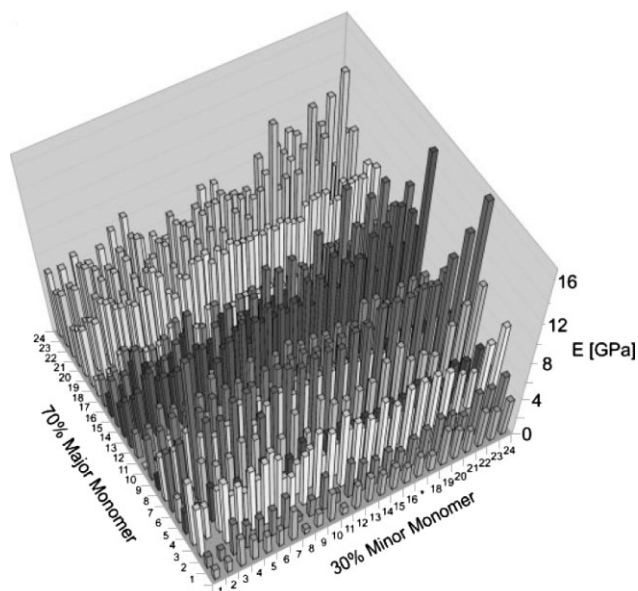


Figure 5. Elastic moduli obtained for a polymer library with 576 members by automated indentation. Reproduced with permission from [12].

2 and 3). Each polymer spot weighed only approximately 1 μg . The 576 unique polymer compositions were subsequently tested by DSI (step 4) in 24 h (Fig. 5). The authors observed that the modulus obtained for the copolymers was not always the value expected from the volume fraction and modulus of its pure constituents, because microstructural and phase changes influenced the stiffness as well. HTE is a suitable technique to investigate the effect of such complex and not yet quantitatively understood factors on the resulting properties. Simon et al.^[14] deposited a gradient library starting from two solutions, one containing poly(L-lactic acid) and the other containing poly(D,L-lactic acid). Subsequently, the composition as a function of location along the deposited film was verified by Fourier transform infrared spectroscopy, and the stiffness was probed as a function of location on the film (i.e., as a function of composition). A higher poly(L-lactic acid) content resulted in a higher crystallinity (as observed by polarized optical microscopy) and a higher modulus. Lin-Gibson et al.^[77] studied photopolymerization of dimethacrylate networks using two-dimensional gradient samples varying in monomer composition and light exposure time. A good correlation was found between the conversion (determined by near-infrared spectroscopy) and the mechanical properties obtained by dynamic DSI measurements for the crosslinked networks. Another study using DSI systematically investigated diblock copoly(2-oxazolines), where a side group is attached to each monomer unit.^[15] Employing four different side groups, all 12 block copolymers and four homopolymers were studied. The surprisingly high stiffness of some of the polymers at low relative humidity could be attributed to intermolecular interaction additional to the van der Waals interaction that usually governs the elastic modulus of glassy polymers. The degree of softening with relative humidity depended on the side group. For one combination of two side groups (ethyl and nonyl side groups), different compositions and two different distributions of the side groups over the polymer

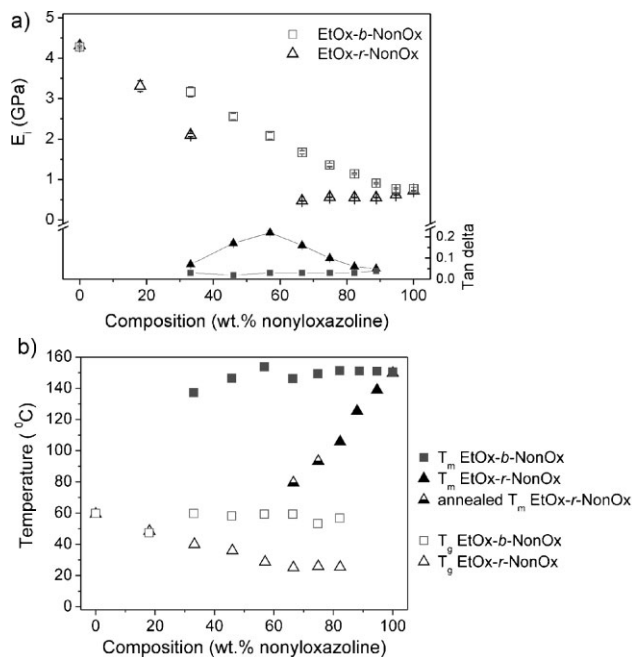


Figure 6. a) The quasi-static elastic modulus (open symbols) and the loss tangent (closed symbols) of block (squares) and random (triangles) ethyloxazoline-nonyloxazoline copolymers are well explained by the phases identified by DSC. b) Two library members exhibited extensive creep (impeding determination of the quasi-static elastic modulus), which reflects their low T_g and the absence of a crystalline fraction. Reproduced with permission from [78]. Copyright 2007 American Chemical Society.

chain (block versus random) were studied.^[78] The observed material stiffness and loss tangent were well explained by the phases identified through differential scanning calorimetry (DSC, Fig. 6). A glass transition well above room temperature indicates the presence of a hard amorphous fraction, a glass transition at or below room temperature indicates the presence of a soft fraction, and a melting temperature above room temperature indicates the presence of a crystalline phase. The observed loss tangent and material stiffness were in line with these expectations, see Figure 6.

Depending on the application one has in mind, the combinatorial experiment involves the screening of more than just the mechanical properties. Therefore, step 4 in the protocol mentioned above may involve several substeps. Anderson et al.^[13] screened a library for both biodegradability and mechanical stiffness. The latter property was determined by DSI. They showed that it is possible to tune both properties independently. Brocchini et al.^[79] established relationships between the chemical structure of 112 distinct polyarylates and their properties such as glass transition temperature, air–water contact angle, and cell proliferation, and subjected selected polyarylates to miniaturized tensile testing as well. Such a combinatorial study not only helps to identify structure–property relations for complex and poorly understood phenomena such as cell adhesion, but also provides a large reference dataset that helps to identify the right material exhibiting the desired combination of properties.

To conclude the discussion on the mechanical property investigation (step 4 in the short description of the combinatorial

cycle), three alternative HTE screening techniques are briefly discussed. Stafford et al.^[80] developed a method to obtain the elastic modulus of polymer films from the buckling wavelength of bilayers consisting of a stiff, thin polymer film with known thickness coated onto a relatively soft, thick substrate. If a composition gradient is present in the film, this technique provides the modulus as a function of composition.^[81] Another instrument for high-throughput mechanical characterization probes the force exerted by a clamped polymer membrane onto a pin.^[82] Discrete polymer samples were generated by clamping a temperature^[83] or composition^[84] gradient film between perforated plates and performing the experiment at each hole. This setup allows for high-strain-rate or low-strain-rate testing, respectively, by either letting the sample plate impact onto the pin or moving it towards the pin using a motorized actuator. A film thickness of 25 μm and a hole diameter of 3 mm was reported,^[83] indicating that at least 200 μg of material is required for each library member. In agreement with analytical modeling, the moduli obtained by this (biaxial) test are 35% higher than the uniaxial moduli for the same materials.^[82] The film-buckling method and the pin-on-film method both require a good control of the film thickness over relatively large distances (or, at least, good knowledge of the film thickness as a function of location).^[81,82] The sample preparation for DSI seems less demanding. Furthermore, both methods start from a gradient library. Therefore, an accurate conversion from property as a function of location to property as a function of composition is necessary. The accuracy of this conversion, which was rather good for the materials investigated by Simon et al.,^[14] depends strongly on the materials and on the (spectroscopic) technique used. For discrete libraries, the conversion from sample position to composition is more straightforward.

Kossuth et al.^[85] measured the complex modulus of elasticity and the loss tangent for 96 samples with the “standard” HTE format (8×12 samples, spaced 9 mm apart) in parallel. Polystyrene-*block*-polybutadiene-*block*-polystyrene was deposited on a polyimide substrate, and on each spot a pin imposed a displacement oscillation while the force was measured. The sample properties could be determined for a temperature range from -120 to 200 °C from the mechanical response of the sample–polyimide “composite”. Apart from a reproducibility study, also the specific softening of the polystyrene phase upon addition of a plasticizer, and the effect of tackifier addition, was demonstrated. Parallel experimentation provides a potentially higher throughput than DSI, which is performed sequentially. However, the parallel approach did cause nonnegligible variation in the modulus as a function of the location of the position on the sample plate.^[85] Using the same probe for all the members of the HTE-library improves the sensitivity of the combinatorial experiment for variations in stiffness through the library. In this context it is noted that the testing rate attainable by DSI (Tweedie et al.^[12] reported testing 576 distinct polymers within 24 h) is sufficiently fast for most combinatorial experiments.

4. Sample Preparation

A convenient sample preparation method is to print or pipette a solution of the polymer onto a substrate and to subsequently dry

the polymer. Usually a stiff substrate such as glass is chosen^[12,14,15] to avoid extra compliance that needs to be corrected for. This approach allows the preparation of both discrete^[15] and gradient libraries.^[14,77] The deposited polymer spot or film needs to be thick enough. For too thin films, the indentation load–displacement response, and therefore the obtained material properties, will be influenced by the properties of the substrate. Influence of the substrate on the obtained hardness can generally be ignored if the film thickness is more than approximately ten times the maximum indentation depth (the exact factor depends on the film and substrate properties^[86–88]), while for the elastic property a somewhat larger factor should be used, as the elastically strained zone extends deeper into the material than the plastically deformed zone.^[24,33] Models have been developed to correct for the substrate influence if the thickness is precisely known,^[87] but such corrections encompass a significant amount of extra work, namely measuring the thickness, repeating the indentation experiments to various depths and extra data processing, which should be avoided during HTE.

Upon depositing films or dots from a solution, the so-called coffee-drop effect may occur. This means that, during drying, material collects at the rim of the spot, leaving only a thin film at the middle of the spot (see Fig. 7a).^[89,90] In the center, the film can be too thin to perform accurate measurements (due to the substrate effect). Furthermore, extensive coffee-drop effect results in height variations on individual samples and between samples of the same library. This significantly increases the time necessary to program and perform a measurement run. Several approaches can be followed to decrease the coffee-drop effect:

- Use a mixture of two solvents with a difference in boiling temperatures and solubility with respect to the polymer (Fig. 7).^[91]
- Increase the polymer concentration in the polymer solution.

- Increase the temperature of the substrate onto which the solution is dropcast or printed.
- Change the substrate surface-energy^[90] or confine the solution.

Another consideration relating to the sample preparation is that the surface should not be tilted, that is, the sample surface should be perpendicular to the indentation axis. We note that a moderate degree of coffee-drop effect may be beneficial, as in that case, indenting somewhat off center of the drop results in a smaller tilt than if no coffee-drop effect occurred at all.

The removal of the solvent from the polymer dot (including the high-boiling solvent that one may have used to optimize the dot shape as discussed above) is a crucial factor because residual solvent may have a large influence on the mechanical properties. Assurance that all solvent is removed can only be obtained if the sample is heated above the glass transition temperature of the polymer, although prolonged drying at temperatures below the glass transition temperature in vacuum will already suffice for thin films or dots deposited using low-boiling solvents. Depending on the solvent used, it may be necessary to perform the drying above the boiling temperature of the solvent and/or in vacuum. The thermal treatment can influence the mechanical properties. Therefore, indentation and DSC experiments may be repeated after a thermal treatment to improve the understanding of the relation between molecular architecture, phase behavior, and mechanical properties.^[78]

It should be realized that the effect of the same thermal treatment on the degree of crystallization, removal of solvent, yield stress increase, etc. will vary through the library, as the distance of the annealing temperature to the crystallization temperature or the glass transition temperature differs for different library members. Repeating the high-throughput experiment after multiple thermal histories opens the way to obtain structure–processing–property relationships for the materials studied.

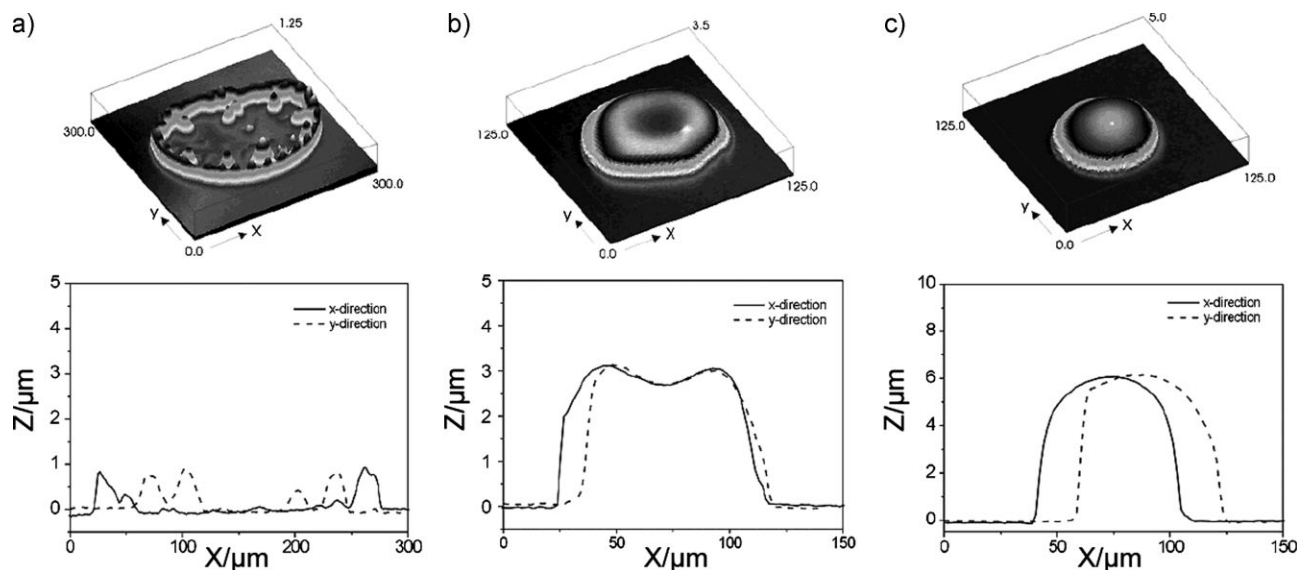


Figure 7. Confocal optical scanning microscopy images and cross sections in the *x*- and *y*-directions of polymer dots resulting after ink-jet printing 1% solutions of polystyrene from a) ethyl acetate, b) acetophenone, and c) a 80/20 wt% ethyl acetate/acetophenone mixture. Reproduced with permission from [90]. Copyright 2004 American Chemical Society.

6. Conclusion and Outlook

In recent years, significant progress has been made in the application of depth-sensing or instrumented indentation as a tool for high-throughput screening of mechanical properties. Impressive throughputs, in terms of the number of samples in only short measurement time, have been reported. The best agreement between elastic modulus, creep parameters, loss tangent and yield stress derived from indentation and their macroscopic counterparts has been obtained by low-throughput experiments, requiring much experimental time per sample and/or considerable modeling effort, such as (reverse) finite element analysis. However, in view of the versatility of the indentation technique, which offers much freedom in experimental protocols and allows for automated post-test surface imaging and use of multiple indenter geometries, and the progress in data analysis, there is ground for optimism that the match between high-throughput indentation results and the macroscopic properties of the material under study will improve. This holds not only for the modulus of elasticity, but also for the creep parameters and the yield stress.

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