Applications of indentation on polymers

Relevant for: UNHT^3, NHT^3, MHT^3, polymers, creep, DMA

Polymeric materials have traditionally been characterized by large scale test instruments such as tensile testing or compression. However, with the development of new polymeric materials, more local testing methods are now required. Among the most important mechanical properties belongs elastic modulus as well as creep and viscoelastic properties. Many polymers also have special surface treatments or are applied in form of surface coatings and paints. Instrumented indentation has successfully been applied for various types of measurements in all these areas. This application report presents typical applications of nanoindentation for characterization of viscoelastic, creep and temperature dependent properties of polymers.

Figure 1 – Table Top UNHT^3 is an excellent tool for both dynamic and creep testing of polymers thanks to its almost non-existent thermal drift.

1 Introduction

Instrumented indentation and mainly nanoindentation has been used for characterization of polymers in several areas, mainly for determination of their viscoelastic properties. These properties can easily be studied by nanoindentation in form of either dynamic mechanical testing (Sinus mode on Anton Paar nanoindenters) or by creep measurements [1,2]. The great advantages of using nanoindentation for testing of polymers are mainly:

1) Small size of the sample,
2) Characterization in small volumes,
3) Possibility to perform creep and dynamic measurements.

Indeed, nanoindentation requires only small samples that are usually easier to obtain than large, bulk samples. Furthermore, many samples are available only in form of films or sheets and their testing by conventional test machines is complicated.

The nanoindentation is applying low loads (in the range of ~0.01 mN up to ~500 mN), which results in small indentation depths. The results (hardness, elastic modulus, viscoelastic properties, etc.) are obtained from small volumes and the measurements are thus very local. Nanoindentation can therefore be used for testing of small samples or areas such as films, coatings, surface treatments of polymers or various microstructures.

The Ultra Nanoindentation Tester (UNHT^3) and the Nanoindentation Tester (NHT^3) can perform both Sinus mode and creep measurements or relaxation measurements, which is used for determination of viscoelastic and creep properties. In addition, both UNHT^3 and NHT^3 can be used for local stress-strain characterization using spherical indenters. All these methods are widely used in polymer industry for characterization of polymers.

This application report presents several applications of nanoindentation for characterization of polymers. The main part is dedicated to characterization of viscoelastic properties of polymers but the nanoindentation stress-strain technique as well as indentation at elevated temperatures are mentioned.

2 Dynamic mechanical analysis – Sinus mode: local characterization of storage modulus, loss modulus and tan δ of polymers

The Sinus mode is used for determination of storage, loss moduli and tangent δ of polymers. This oscillation mode is usually applied during hold period at constant force (it is recommended to include a creep phase before the Sinus measurement to reach stable conditions, Figure 2). In such condition the depth

change is minimal and the storage and loss moduli are measured at almost constant depth.

An example of such indentation are measurements on PVB (Polyvinyl butyral) that have been done using the UNHT^3. Berkovich indenter, maximum load of 0.5 mN, frequency of 5 Hz and amplitude of 0.02 mN was used for all these measurements.

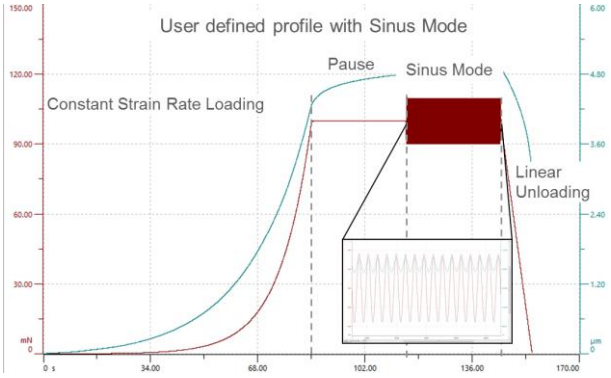

Figure 2 – Typical loading profile for Sinus mode measurement on polymers.

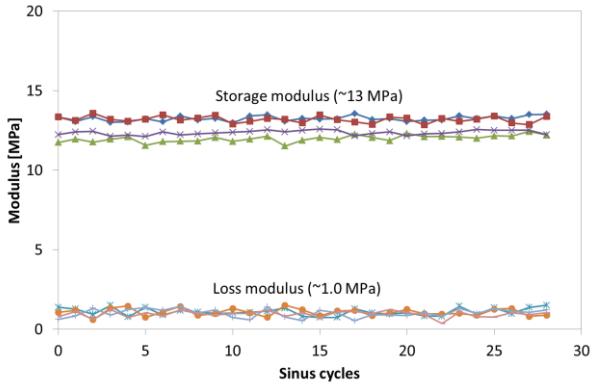

Figure 3 – Typical loading profile for Sinus mode measurement on polymers (PVB sample).

The PVB sample was tested in frame of a larger study where more polymeric sheets with various properties were tested (Figure 4):

- Polyether ether ketone/acrylate/polyether ether ketone (Loudspeaker laminate),
- Hydrated nitrile butadiene rubber (HNBR),
- Polyethylene therephtalate/polyethylene therephtalate/fluor coating (PPV Backsheet),
- Thermoplastic silicon elastomer (TPSE).

Some of the polymeric samples were very soft and adhesive. These samples had to be tested using a special Adjustable sample holder where the active reference of the UNHT^3 is placed on an aluminum block. Such samples can also be tested with the Bioindenter.

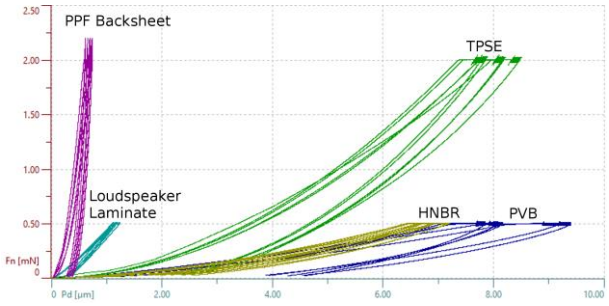

Figure 4 – Comparison of Sinus mode tests on five polymeric sheets: TPSE Encapsulant, Loudspeaker laminate, PPF Backsheet, PVB and HNBR.

3 Creep measurements

Creep measurements are especially useful when long term viscoelastic properties have to be determined. This is particularly interesting for computer modeling which is used in prediction of long term stability of components using polymeric materials. An indentation creep measurement consists of fast loading and a long hold at constant force, where the increase of depth (creep) is monitored. The loading usually takes several seconds whereas hold period should be much longer than the loading time (usually 10 to 20 times the loading times). When spherical indenter is used, the Anton Paar Indentation software allows fitting of the creep data and so the instantaneous and infinity shear moduli as well as partial compliances and the retardation times are obtained. An example of creep fit following the method published in [3] is shown in Figure 5.

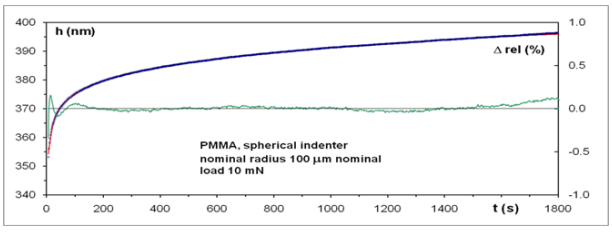

Figure 5 – UNHT^3 Creep measurement with fit and residuals (Δ rel) on polyacrylamide (PMMA). Maximum load 10 mN, duration of creep 1800 s, depth increase during hold ~30 nm.

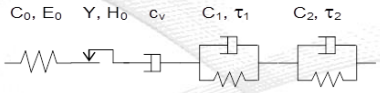

Figure 6 – Material model used for description of viscoelastic properties of polymers during creep (version with two Kelvin-Voigt bodies).

The fit of the creep data in Figure 5 was done with three Kelvin-Voigt bodies using the following formula:

$$[h(t)]^m = KP\left\{C_0 + \sum C_j\left[1 - \rho_j e^{-\frac{t}{t_j}}\right]\right\}$$

Where *m* is 3/2 for spherical indenter, K is 3/(4√R), *P* is load, C_0 is instantaneous compliance, C_j and τ_j are compliances and retardation (relaxation) times of the Kelvin-Voigt bodies and the term ρ_j is the ramp correction factor [2,4]. For the example shown in Figure 5 the depth increase in 1800 s was ~30 nm: this implies that only an instrument with excellent thermal stability can be used for this type of measurements. This is the case of the UNHT^3, which has almost non-existent thermal drift (≤ 0.05 nm/min, [5]). The measurements showed in Figure 5 were part of large creep study on PMMA where different loads were used to simulate contact pressures from 25 MPa to 156 MPa. Under these pressures the PMMA remains viscoelastic (without plastic deformation). The results (Table 1) show that the reduced elastic modulus values are consistent at loads of 5 mN to 50 mN and that the creep fit is therefore simulating well this material. As for the lower value of E_r at 1 mN, this is probably due to some uncertainty in the creep fit for such small depth increase (the creep was only ~8 nm in 30 minutes)

Table 1 - Results of PMMA creep fit at different loads.

	C_0 (nm/N)	τ_1 (s)	τ_2 (s)	τ_3 (s)	E_r (GPa)
1 mN	0.39	8	67	4977	2.57
5 mN	0.29	5	38	727	3.42
10 mN	0.28	14	112	1156	3.62
50 mN	0.26	15	112	994	3.78

4 Stress-strain characterization of polymers

Although the majority of applications of nanoindentation of polymers concerns viscoelastic properties (either by Sinus mode or creep measurements), also stress-strain measurements have been applied to polymeric materials. This indentation method is usually used when only thin sheets of polymers are available or when the polymer contains different phases which have to be characterized individually. An example of indentation stress-strain curve on polymer is shown in Figure 7. Note the excellent repeatability of the results: this is mainly due to the fact that larger indentation depths were used and the effects of surface roughness were thus minimized. The NHT^3 Nanoindentation Tester was used for these measurements because it provides large force range to test both in the elastic and plastic regime. For lower loads or softer samples, the Ultra Nanoindentation Tester (UNHT^3) can be used as it offers excellent thermal stability.

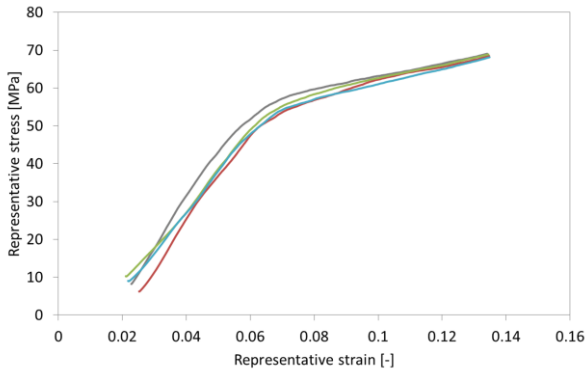

Figure 7 - Comparison of indentation stress-strain curves on a polymer (NHT^3 with R = 20 µm spherical indenter, measurements in Sinus mode).

The presented indentations were performed with 20 µm radius spherical indenter and maximum load of 100 mN using constant strain rate loading at 0.05 s^{-1}. The yield stress was estimated to be approximately 55 MPa.

5 Measurements of properties of polymers at elevated temperatures

Nanoindentation at high temperatures is a specific topic which requires more advanced test conditions (vacuum, special sample holder with heating, etc.). However, polymers can quite easily be tested using the UNHT^3 instrument at temperatures up to 200°C. These tests require use of thermal shield on the UNHT^3 head by a water cooling block and sample heating (Figure 8). This configuration is particularly suitable for testing of polymers where the maximum test temperatures (e.g. glass transition temperature) are generally below 200°C.

Figure 8 – The UNHT^3 with water cooling block and the 200°C heating module.

An example of nanoindentation of polymer (PMMA) at temperatures up to glass transition temperature (~105°C) is shown in Figure 9. The sample was indented at increasing temperatures from room temperature (25°C) up to 110°C (temperature was measured at the top surface of the sample).

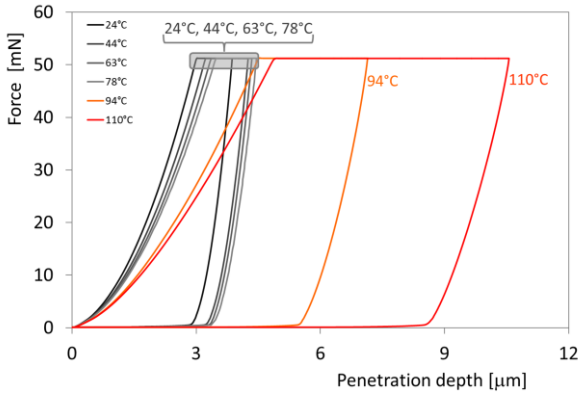

Figure 9 – Nanoindentation of PMMA at different temperatures. Note large increase in penetration depth as well as increase of creep at 94°C and 110°C.

Table 2 - Indentation elastic modulus (E_{IT}) of PMMA at different temperatures.

	24°C	44°C	63°C	78°C	94°C	110°C
EIT [GPa]	4.4	3.9	3.6	3.4	1.3	0.7
	4.5	3.9	3.6	3.4	1.3	0.7
	4.4	3.9	3.6	3.4	1.4	0.7
Average	**4.4**	**3.9**	**3.6**	**3.4**	**1.3**	**0.7**
St dev	0.0	0.0	0.0	0.0	0.1	0.0

A small increase indentation depth was observed at temperatures up to ~80°C. At 94°C and 110°C however, the instantaneous penetration depth as well as creep (depth increase during hold period) increased much more: this was due to temperature being close (and above) the glass transition temperature. At this temperature the polymer abruptly changes its viscoelastic properties.

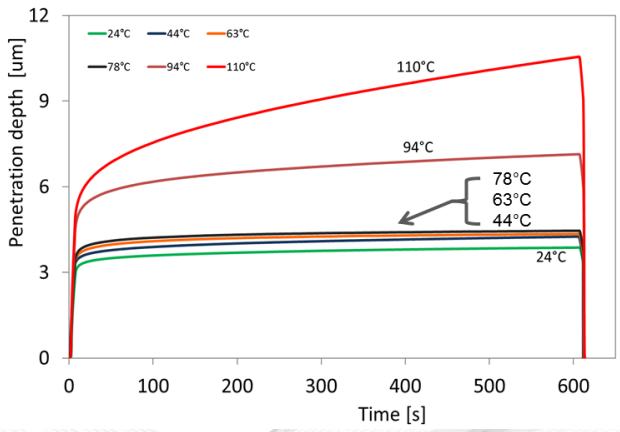

Figure 10 – Creep data (penetration depth increase during 10-minutes hold at constant force). Note large increase at 94°C and 110°C.

This is characterized by significant decrease of elastic modulus (Table 2) and more important creep. The evolution of creep itself can be observed more easily when the depth is plotted as a function of time (Figure 10). This figure shows clearly that the largest changes in elastic and creep properties occur close the glass transition temperature whereas below this temperature the effects of temperature are much less pronounced.

6 Conclusions

This application report presents several examples of the use of nanoindentation for characterization of polymers. Among the main applications belong dynamic measurements using the Sinus mode and creep measurements. The Sinus mode indentations are used to reveal viscoelastic properties by the measurement of the storage, loss moduli and tangent δ. The data from creep measurements can be fitted and the values of instantaneous, infinity shear and elastic modulus as well as relaxation times are obtained. These results are important for prediction of long term behavior of polymeric materials and the fit method is implemented in the Indentation software. Nanoindentation can also be used for determination of an indentation stress-strain curve on polymers, especially of thin polymeric samples. Thanks to its excellent thermal stability, the UNHT^3 can be used for measurement of viscoelastic properties of polymers at elevated temperatures up to 200°C.

7 References

1. Herbert EG, Oliver WC, Pharr GM. Nanoindentation and the dynamic characterization of viscoelastic solids. J Phys Appl Phys. 2008;41:074021.

2. Oyen ML. Spherical indentation creep following ramp loading. J Mater Res. 2005;20:2094-2100.

3. Cook RF, Oyen ML. Nanoindentation behavior and mechanical properties measurement of polymeric materials. Int J Mater Res. 2007;98:370-378.

4. Nohava J, Menčík J. A contribution to understanding of low-load spherical indentation-Comparison of tests on polymers and fused silica. J Mater Res. 2012;27:239-44.

5. Hou XD, Jennett NM. Defining the limits to long-term nano-indentation creep measurement of viscoelastic materials. Polym Test. 2018;70:297-309.

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