JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 10, No. 12, December 2008, p. 3288 - 3291

Determination of viscoelastic properties by nanoindentation

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Indenter penetration into viscoelastic materials depends on the load magnitude and history of loading. Hardness is not a constant, but decreases with the time under load. Corrections must be made in the unloading curve used for the determination of contact area and „instantaneous" elastic modulus. The viscoelastic properties are best characterised by means of rheologic models consisting of springs and dashpots. The constants in these models can be obtained easily from the time course of indenter displacement under constant load, but one must respect also the deformations occuring during the load increase from zero to the nominal load. The paper explains the principle of instrumented indentation, gives the theory and formulae for elastic-plastic and viscoelastic materials, and describes the practical procedure for testing and data evaluation.

(Received October 4, 2008; Accepted November 27, 2008)

Keywords: Mechanical properties, measurement, indentation, nanoindentation, hardness, viscoelasticity, elastic modulus

1. Introduction

Nanoindentation, called also depth-sensing or instrumented indentation, provides information about mechanical properties from indenter load and depth measured continuously during loading and unloading (Fig. 1). Today, these methods are well established for elastic-plastic materials like metals or ceramics. They can also be used for the characterisation of polymeric and other materials whose response to load depends also on time, but specific features of their behaviour must be taken into account in the preparation of tests and data evaluation. The pertinent methods are still under development. This paper, after a brief review of basic formulae for nano- indentation into elastic-plastic materials, explains the load response of viscoelastic materials and presents the general formulae, with emphasis on indentation testing. Also, a practical testing procedure is described.

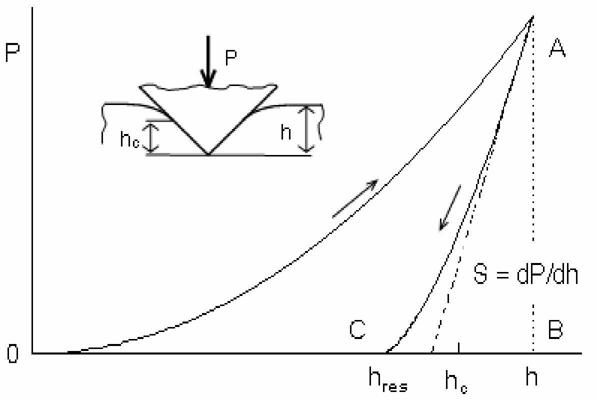

Fig. 1. Load-depth curves of an indentation test – a schematic.

2. Principal formulae for depth-sensing testing of elastic-plastic materials

In depth-sensing tests, hardness H is defined as the mean contact pressure, and calculated by dividing the indenter load P by the projected contact area A:

$$H = P / A \quad . \tag{1}$$

The contact area is calculated from contact depth h_c, obtained from the total penetration h, indenter load and contact stiffness $S = \mathrm{d}P/\mathrm{d}h$ at the beginning of unloading (Fig. 1):

$$h_c = h - \varepsilon P/S \quad , \tag{2}$$

where ε is a constant ($\varepsilon \approx 0.75$). The stiffness S is determined from the regression function fitted to the unloading curve, usually by the procedure proposed by Oliver and Pharr [1]. Then, the reduced modulus E^* is calculated from the contact stiffness and contact area:

$$E^* = \pi^{1/2} S / (2\beta A^{1/2}) \tag{3}$$

β is the correction factor for the indenter shape ($\beta \approx 1.05$). E^* is related to the elastic modulus E and Poisson ratio ν of the specimen (no subscript) and indenter (subscr. i) as

$$1/E^* = (1 - \nu^2)/E + (1 - \nu_i^2)/E_i \quad . \tag{4}$$

3. Theoretical background for testing of viscoelastic materials

The response of some materials, such as polymers, is more complex, as it depends not only on the load magnitude, but also on its duration and time course.

The indenter continues penetrating into the specimen even under constant load (Fig. 2). Such materials are called viscoelastic or viscoelastic-plastic. In this case, hardness (1) is no more a constant, but decreases with the time under load, $H = H(t)$.

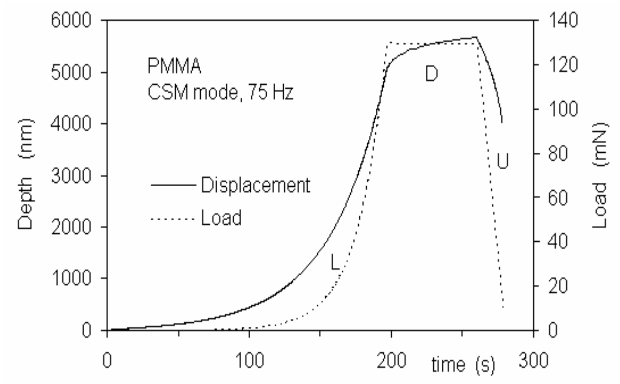

Fig. 2. Time course of a nanoindentation test into PMMA [2]. L – loading, D – dwell under constant load, U – unloading.

Moreover, due to delayed deforming also the unloading part of the $P - h$ curve is sometimes distorted (Fig. 3); it is much more convex than in elastic matrials, with a bulge or even a "nose". This can lead to an error in the determination of contact stiffness S, and thus to an error in the contact depth and area, as well as in the elastic modulus and hardness. If the time-dependent effects are not negligible, a special approach is needed. This paper will deal with procedures for viscoelastic materials and monotonic loading and unloading. The determination of viscoelastic properties under harmonic loading can be found in Menčík et al. [2]. The characterisation of viscoelastic-plastic properties, typical by the occurrence of time-independent permanent deformations, will be the topic of another paper.

The delayed deforming can be accounted for in various ways. In order to avoid the distorsion of unloading curve (Fig. 3), it is recommended to insert a dwell (with constant load) between the loading and unloading period. According to Chudoba and Richter [3], the influence of delayed deforming on the unloading curve may be neglected if the creep velocity has decreased so that the penetration depth at the end of dwell grows not faster than 1% per minute. Some disadvantage of this approach is that the indenter depth at the beginning of unloading (after the dwell) is larger than at the end of loading, and this results in larger contact area and lower apparent hardness.

Therefore, some authors recommend to use relatively fast loading followed immediately by fast unloading, and to calculate the contact depth and elastic modulus using the effective contact stiffness S, defined by the following expression proposed by Ngan et al. [4]

$$S^{-1} = S_{app}^{-1} + \dot{h}_d \Big/ \left|\dot{P}_u\right| \quad ; \tag{5}$$

S_{app} is the apparent stiffness, obtained by the common Oliver & Pharr [1] procedure from the unloading curve, $\dot{h}_d$ is the indenter velocity at the end of dwell, and $\dot{P}_u$ is the load decrease rate at the beginning of unloading (Figure 3); the units are N/m, m/s and N/s, respectively.

However, the results can also be influenced by viscoelastic deforming during the loading phase. What is considered as fast loading with respect to the possibilities of the indentation device, it is sometimes not sufficiently fast regarding the material ability of quick viscoelastic response. Moreover, it is generally insufficient to characterise materials that flow permanently under load, only by means of a single value of hardness or elastic modulus. Preferrably, the time-dependent properties should be described in a more appropriate way. Usually, rheological models consisting of springs and dashpots are used, such as the Kelvin or Maxwell model and their combinations (Fig. 4). The parameters in these models, suitable as material characteristics, can be obtained by fitting the time course of penetration depth by a suitable creep function, depending on the material, indenter shape and loading history. The commonly used formulae are based on the approach proposed by Lee and Radok [5], which uses the elastic solution, but replaces the elastic constants by a viscoelastic hereditary integral operator; cf. Johnson [6] or Oyen [7].

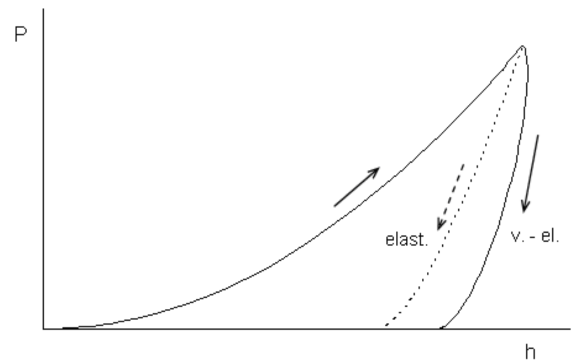

Fig. 3: Load-depth diagram for elastic and viscoelastic (v.- el.) material; note the differences between unloading curves.

The relationship between indenter load and depth of penetration into an elastic or viscoelastic material under monotonic loading can be expressed generally as

$$f[h(t)] = K\,\psi(P, J, t) \quad , \tag{6}$$

where f is some function of the indenter shape and penetration, K is a constant characterising the indenter geometry, and $\psi(P, J, t)$ is a function depending on the load magnitude and history, on material parameters, and on time. For spherical indenter (subscript s),

$$f_S = h^{3/2} \;;\; K_S = 3 / [\,4\sqrt{R}\,] \;; \tag{7}$$

R is the indenter tip radius. For pointed indenters (conical, Berkovich or Vickers, subscript c),

$$f_C = h^2 \; ; \; K_C = \pi / [\, 4 \tan\alpha] \; ; \qquad (8)$$

α is the semiangle of indenter tip or of equivalent cone.

The function ψ for ideally elastic materials is:

$$\psi = P(1-\nu)/G \; ; \qquad (9)$$

G is the shear modulus, ν is Poisson ratio. The general formula for linearly-viscoelastic materials is

$$\psi(t) = \int_0^t J(t-u)[dP/du]du \quad , \qquad (10)$$

where $J(t)$ is the so-called creep compliance function, depending on the material model used, t is time, and u is a dummy variable for integration. For constant load after step change from 0 to P, the function ψ is simply the product of load and creep compliance function,

$$\psi(t) = P\,J(t) \quad . \qquad (11)$$

However, step load is impossible to realise; there is always some period of load increase. For ramp loading with constant load rate, $R = dP/dt = const$, it holds

$$\psi(t) = R\int_0^t J(t-u)du \quad . \qquad (12)$$

The penetration under constant load P following ramp load lasting t_R can be described by the function

$$\psi(t) = R\int_0^{t_R} J(t-u)du \quad . \qquad (13)$$

where t_R is the duration of load increase. Formula (13), valid for $t > t_R$, was obtained as the sum of two loads growing with the constant rate R: the first load starts at $t = 0$, while the other, acting in the opposite direction, starts at time t_R. Thus, for $t > t_R$, the load is constant, $P = Rt_R$.
The application of the above formulae can be illustrated on a relatively universal model, consisting of a spring in series with a Kelvin-Voigt unit (Fig. 4), which

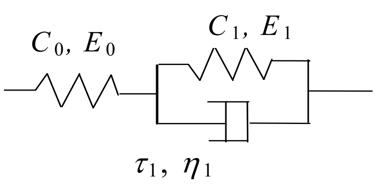

Fig. 4. Standard Linear Solid (a schematic).

is a spring in parallel with a dashpot. For this model, called Standard Linear Solid, the creep compliance function is

$$J(t) = C_0 + C_1 [1 - \exp(-t/\tau_1)] \; , \qquad (14)$$

where C_0 and C_1 are compliance constants, and τ_1 is so-called retardation time. This is a time constant of the system, related to the compliance C_1 of the spring and viscosity η_1 of the dashpot in the Kelvin-Voigt body as $\tau_1 = \eta_1 C_1$. A more complex response can be approximated using more Kelvin-Voigt units in series,

$$J(t) = C_0 + \sum C_j [1 - \exp(-t/\tau_j)] \; , \qquad (15)$$

($j = 1, 2,\dots n$). The instantaneous compliances C_j are related to the shear moduli G_j and Poisson ratios ν_j by

$$C_j = (1-\nu_j)/G_j \; . \qquad (16)$$

The springs can be characterised also by means of tensile moduli E, related to the shear moduli as

$$E_j = 2(1+\nu_j)\,G_j \; . \qquad (17)$$

However, only G_0 and E_0 correspond to the actual (instantaneous) elastic modulus of the material. The other constants C_1, C_2… just characterise delayed deforming. The "moduli" G_1, G_2… or E_1, E_2… do not represent additional stiffnesses, but reciprocals of additional, time- dependent compliances.

Indentation creep under constant load P following ramp loading (with constant load rate) lasting $t_R = P/R$, can be described by the function derived by Oyen [7]:

$$\psi(t) = P\,\{\, C_0 + C_1 [1 - \rho_1 \exp(-t/\tau_1)]\} \; , \qquad (18)$$

or, for a generalised standard linear solid (15),

$$\psi(t) = P\,\{\, C_0 + \sum C_j [1 - \rho_j \exp(-t/\tau_j)]\} \; . \qquad (19)$$

In expressions (18) and (19), ρ_j is so-called ramp correction factor, calculated as [7]:

$$\rho_j = (\tau_j/t_R)\,[\exp(t_R/\tau_j) - 1] \; . \qquad (20)$$

Note that the formulae (18) and (19), valid for $t \geq t_R$, differ from those for step loading, based on Eqs. (14) and (15), only by the factors ρ_j at the exponential terms. For fast loading, with the load increase very short compared to the retardation time, $t_R \ll \tau_j$, the ramp correction factor is close to 1; it attains 1.025 for $t_R/\tau_j = 0.05$ and 1.05 for $t_R/\tau_j = 0.1$, and grows rapidly for higher ratios t_R/τ_j.
REMARK. Creep compliance function (15) can also be written in another form [7]:

$$J(t) = C_0' - \sum C_j \exp(-t/\tau_j) \; , \qquad (21)$$

where

$$C_0' = C_0 + \sum C_j \; . \qquad (22)$$

C_0' expresses the asymptotic compliance, corresponding to very long loading ($t \to \infty$), in contrast to C_0 that characterises the instantaneous compliance, i.e. the immediate reaction to sudden loading. Similarly, Eq. (19)

can be written as follows:

$$\psi(t) = P\,[C_0' - \sum C_j \rho_j \exp(-t/\tau_j)]\,. \quad (23)$$

In the limit case with j = 1, formulae (21) and (23) correspond to the Standard Linear Solid (15) and (18).

4. Practical part

A suitable procedure for the determination of material parameters is as follows. The indenter is loaded quickly (with the constant load rate R) to the nominal load P, then kept under this load for a relatively long time, and unloaded quickly. From the unloading curve, the contact stiffness is determined, either directly as $S = \mathrm{d}P/\mathrm{d}t$ if the indenter velocity at the end of dwell was negligible, or using correction (5). The contact area A, necessary for the determination of instantaneous elastic modulus E_0 from the unloading curve via Eqs. (3) and (4), is calculated from the contact depth h_c, determined by Eq. (2) from the depth h at the beginning of unloading.

The dwell under constant load can be used for the determination of constants in rheological (spring and dashpot) models. Depending on the model, the function $\psi(t)$, defined by Eq. (18) or (19), is inserted into (6), together with the function f and constant K, chosen from Eq. (7) or (8) with respect to the indenter shape. This function $f[h(t)]$ is then used to fit the measured $h(t)$ data.

The constants C_0, C_1, τ_1, ρ_1, etc. can be obtained by minimising the sum of squared differences between the measured and calculated $h(t)$ values. A suitable tool for this purpose is the facility Solver in some programs, e.g. Excel. However, the actual procedure must be modified for the following reason. The constants C_j appear in Eqs. (18), (19) and (23) only together with the constant ρ_j (as product $C_j\rho_j$), or together with the constant C_0 (as C_0', cf. Eq. 22). Thus, the regression fitting of experimental data can yield the correct values of ($C_j\rho_j$) and C_j', while the individual values of constants C_j can be wrong. The constants C_j, however, are the genuine material parameters, independent of the loading history, and must be determined accurately. Their correct values can be obtained using a simple three-step data processing, based on the verified fact that the retardation times τ_j can be determined correctly for any mathematical form of the model (23).

In the first step of the procedure, the $h(t)$ data obtained by indentation during the constant-load part of the test are fitted by the function (23), with all constants C_0, C_1, τ_1, ρ_1, etc. considered as "free". In this way, the retardation times τ_j are obtained. Then, the ramp correction factors ρ_j are calculated from Eq. (20) for these times τ_j and the duration t_R of the load increase. These values ρ_j are then inserted as fixed constants into Eq. (23) or (19), and the curve fitting, now searching for the remaining constants C_0, C_1, τ_1, etc. is done again. Computer modelling has shown that this procedure yields correct results.

From the compliances C_0, C_1, etc., it is also possible to calculate the values of G_0, G_1, etc. (or E_0, E_1…) for the (chosen) value of Poisson ratio ν. In an ideal case, the instantaneous shear modulus G_0 is related to the (instantaneous) tensile modulus E_0 from the unloading curve as $G_0 = E_0/[2(1+\nu)]$. If the calculated parameters do not fulfil this condition, it is an indication that a correction is necessary, e.g. for the delayed deforming during the load increase period.

It should be reminded here that very complex models, with more than about 6 – 7 regression constants, can sometimes cause problems in the search for their accurate values, and a compromise between the model complexity, accuracy and "robustness" may be necessary. A similarly good fit is sometimes obtained for various arrangements of springs and dashpots. The model complexity should also respect the amount of experimental data available, especially regarding the test duration.

A final remark. Equations (14), (15), (18) and (19) are only valid for reversible viscoelastic deformations, which occur under a spherical indenter (sometimes even under pointed indenter [8]) if sufficiently low load is used. For higher loads, also plastic deformations appear. The characterisation of viscoelastic-plastic materials with permanent deformations exceeds the scope of this paper and will be the topic of another work.

5. Summary

Mechanical properties of viscoelastic materials with time-dependent response can be determined by nano-indentation, which continuously measures indenter load and displacement. The paper has explained the principle of the method as used for elastic-plastic materials, gave the basic formulae for expressing the load response of visco-elastic materials by means of spring-and-dashpot models, and described a procedure for their indentation testing and the determination of material parameters.

Acknowledgement

The work and its presentation were supported by the Grant Agency of Czech Republic under project GAČR No. 101/07/0727.

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