Measurement of mechanical properties of viscous plastic materials by nanoindentation

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Abstract

Nanoindentation is a widely used method for determining mechanical properties, such as hardness, and elastic modulus. Nevertheless, in the case of viscous materials, the time dependent response of the material generates a bulge on the unloading curve that leads to incorrect values of the contact stiffness and thus of the mechanical properties. This paper presents methods developed on two viscoplastic materials (indium and indium-tin eutectic) to measure the elastic modulus and the creep exponent. To fix the bulge problem, we propose to realise cyclic indentations in order to obtain unloading and reloading curves. Results show that the lower parts of these two curves are similar because creep behaviour becomes negligible. Thus, the values of the modulus calculated from the initial slope of the reloading curve are constant and in good agreement with the values obtained from standard tensile tests. Furthermore, a method has been developed to measure the creep exponent. It consists of measuring the contact pressure as a function of the strain rate during hold load plateaux. Experiments show that the average value of the creep exponent (3.7 for the indium-tin eutectic and 7.6 for indium) does not depend on the loading conditions and are in good agreement with values obtained from tensile and torsion tests (3.7 and 7.6 respectively).
Keywords: nanoindentation, cyclic indentation, elastic modulus, creep exponent, viscoplasticity.

1 Introduction

In the two last decades, nanoindentation technique has been widely developed and used for measuring mechanical properties such as elastic modulus and

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doi:10.2495/SECM130101

hardness from load-displacement curves [1]. It becomes a popular method on account of its experimental reliability, rapidity and simplicity. The analysis of unloading curve such as the Oliver and Pharr models [1] allowed the development of methods to calculate elastic modulus and hardness in the case of elastoplastic materials. These methods use the beginning of the unloading curve to compute the contact stiffness, the contact depth and thus the hardness and the elastic modulus using the Sneddon's equation.

Nevertheless, in the case of time-dependent materials, the unloading curve is not a perfect elastic response but the combination of an elastic response to unload and of viscoelastic-viscoplastic to load and unload. Typically, indentation experiments conducted on viscous materials leads to difficulties to measure correctly the mechanical properties. It is for example well-known that unloading curves present a bulge due to viscous behaviour for low unloading rates and-or low hold load times before unloading leading to an impossibility to compute accurately the mechanical properties [2–7].

All materials present a viscous behaviour for temperatures higher than approximately half of their melting points expressed in Kelvin. Thus, this problem is encountered for materials with low melting points as polymers, biological samples [2–7] or metals like Sn-3.5Ag alloys [6] or indium [7]. The development of nanoindentation experiments at high temperatures [8] leads to the generalisation of this problem to all materials. Thus, it is necessary to develop methods that give accurate and reliable measurements of the mechanical properties in the specific case of viscous materials. This paper presents works on the development of methods that allows the measurements of the creep exponent and elastic modulus for materials that exhibit viscoplastic materials. Methods have been developed on two viscoplastic materials indium and indium-tin eutectic at room temperature to avoid specific technical problems of nanoindentation at highs temperatures [8].

2 Materials and methods

2.1 Materials

Materials used in this study are indium and indium tin eutectic. These two materials were chosen for their low melting point, 156°C and 117°C respectively, and for their different structures. Indium of 99.999% purity was from Goodfellow while indium-tin (In %52 – Sn %48) eutectic was from the Alfa Aesar. Materials were fused in a furnace at 200°C in small Pyrex test tubes. Two thermal treatments have been prepared for this study: i) The samples were quenched after been melt in the furnace and ii) The samples were annealed in the furnace. The samples were mechanically polished using increasingly fine SiC wet sandpaper, from 600 through 4000 grit using the minimal load and a rotational speed equals to 60 RPM. A final polishing was performed using a polish cloth with silica colloidal suspension (1 µm) [9].

All experiments have been performed at room temperature with a Berkovich indenter using a G200 nanoindenter from Agilent. The loading and unloading stages have been realized at constant loading rate/load ratio.

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2.2 Elastic modulus method

The measurement of an accurate value of the initial slope of the unloading curves is detrimental for a correct measurement of the elastic modulus. In their original works [1], Oliver and Pharr have pointed out the effect of creep on the beginning of the unloading curve and on the calculus of the stiffness. They suggest an experimental protocol where the sample is load and unload three times and the calculus of the contact stiffness from the initial slope of a power fit of the unloading curve.

For materials having important viscous behaviour, the Oliver and Pharr protocol is generally not adapted and different approaches have been proposed. Hold load stages before unloading and high unloading rates are generally proposed to reduce viscosity effect [2–5]. Feng and Ngan [10] have proposed a formula to recompute the contact stiffness in order to eliminate the creep effects for the case of materials exhibiting linear viscoelasticity. Ngan *et al.* [11] proposed a similar approach in the general case of viscoelasticity. It appears to be a successful way to calculate the elastic modulus for amorphous selenium [11], human dentin [12] and polypropylene [13]. Based on works with finite element simulations, Cheng *et al.* [14] proposed a formula to correct the elastic modulus using a displacement controlled experiment.

Cyclic indentation is another interesting method to calculate the elastic modulus [1, 15–17]. Finite elements simulations [18] predict that the unloading and the reloading curves for elastic-plastic materials should be identical. However, in some materials a hysteresis is observed. The load-displacement curve for nanoindentation presents different slopes for the unloading and reloading curves. In particular, Shuman *et al.* proposed an original method to calculate the elastic modulus, using multi-step indentation tests [15]. They found that the values of the elastic modulus computed from reloading curves were far more constant and reliable that the values computed from unloading curves. Even if the phenomena (creep, friction, residual stress, plasticisation, etc...) at the origin of the hysteresis are not clearly understand, the work of Shuman *et al.* clearly pointed out that the reloading curve rendering a purer elastic behaviour than the unloading curve.

For our particular problem, the loading and unloading curves are always submitted to creep. Equation (4) shows that, during an indentation experiment, the indentation depth rate could only decrease if the stress decreases. For example, during hold load time, the increase of the indentation depth decreases the stress and the indentation depth rate decreases with time. Another more efficient ways to decrease the indentation depth rate is to decrease the stress. The measurement of the contact stiffness by means of the Continuous Stiffness Measurement during partial unloading shows that the contact stiffness is approximately proportional to the indentation depth if the final load is higher than one third of the maximum load [2–3]. Thus, as shown in the next section, an unloading stage reached until a final load equals to one half of the maximum load generates only a small decrease of the indentation depth and then of the contact area. It obviously leads to a decrease of approximately one half of the contact pressure. Because the indentation rate is proportional to the stress at the

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power n, one can deduce than a decrease of 50% of the load will leads to a decrease of indentation rate of approximately 0.5^n. In the case of indium (n=7.6) the indentation depth rate due to creep will be divided by approximately 200 during the unloading stage. Thus one can expect that creep becomes negligible and obtains a pure elastic response on at least, one part of the unloading curve. In this case, the slope of the curves could be used to compute the contact stiffness and the elastic modulus according to the Oliver and Pharr method. Obviously, if the sample is reloaded, the stress will increase and the creep phenomenon should restart. Then we can expect that if the sample is unload and reload, creep occurs only for high loads and become negligible at lower loads. No hysteresis due to creep should occurs in the lower part of the loading-reloading curves whereas a huge hysteresis should be observed at higher loads.

From these considerations, we propose the following protocol. The samples are load at constant loading rate/load ratio equals to 0.05 s^{-1} until an indentation depth equals to 10 µm and followed by a long hold load stage (600s). During these two stages, cyclic unload-reload stages are performed: Five during the load stage (protocol 1 and 3) and ten during the hold load stage (protocol 2 and 3). These cyclic unload-reload stages consist in first, an hold load time of one minute to generate a maximum of creep before unloading, second an unload of 50% of the maximum load, and third a reload to the maximum load (Fig. 1). The aim of these complex protocols is to see if the method is sturdy: The values of the elastic modulus computed from unload-reload curves should be constant whatever the loading and creep history of the sample.

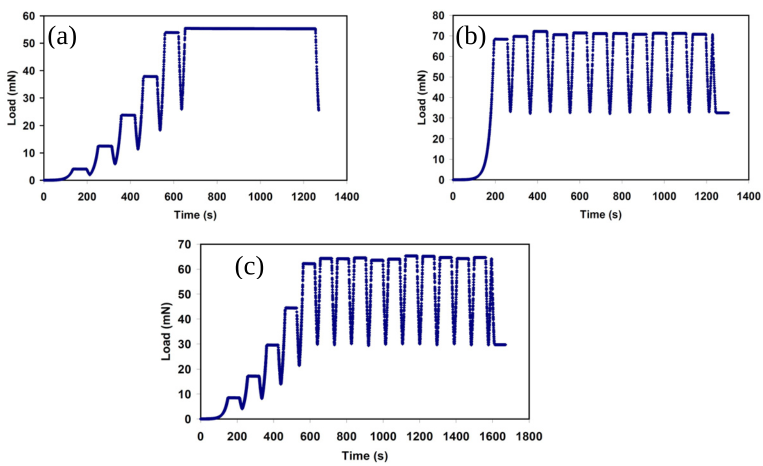

Figure 1: Schematic representation of cyclic unload-reload stages performed during load stage, protocol 1 (a) hold load stage protocol 2 (b) loading and hold load stage protocol 3 (c).

2.3 Creep exponent method

Creep behaviour of material is highly stress dependent: typically, for monoaxial experiments, the strain rate is a power function of the stress:

$$\dot{\varepsilon} = B\,\sigma^{n} \tag{1}$$

where n is the creep exponent, $\dot{\varepsilon}$ is the strain rate whit, σ is a monoaxial stress and B is a pre-exponential constant. This equation could be extended to nanoindentation experiments: It is assumed that the strain rate is proportional to the contact depth rate/contact depth ratio [7]:

$$\dot{\varepsilon} \propto \frac{\dot{h}_c}{h_C} \tag{2}$$

where h_c is the contact depth. The monoaxial stress is replaced by the average contact pressure P:

$$\sigma = P = \frac{L}{A} = \frac{L}{C\,h_c^2} \tag{3}$$

where L it is the load, A is a projected area, and C is a geometrical constant that depends on the geometry of the indenter (24.56 for Berkovich indenters). Thus creep behaviour in the case of nanoindentation experiments should be expressed by the following equation:

$$\frac{\dot{h}_c}{h_c} = B\left(\frac{L}{C\,h_c^2}\right)^{n} \tag{4}$$

Whatever the load, the contact depth should always increase leading to a continuous increase of the contact area. If the load is maintained constant, the increase of the contact area leads to a decrease of the contact pressure. The contact pressure, defined as the hardness for elastoplastic material, is thus no more constant for viscoplastic materials and should not be considered as a pertinent parameter to describe the plastic behaviour of those materials. Thus, the determination of the values of constant B and of the creep exponent n is more pertinent to describe the plastic behaviour of viscoplastic materials and should be determined by nanoindentation if possible.

Several methods could be used to determine the creep exponent by nanoindentation creep.

- The constant depth method or "relaxation test method" consists of maintaining, the indentation depth constant after a loading stage. The load is then adjusted by a servo-loop to keep constant the indentation depth. This method is not popular due to experimental difficulties and to the calculus of the real contact area and contact pressure.
- In Constant Loading Rate (CLR) method, the hardness is computed as a function of the strain rate during loading time [19].
- The constant indentation strain rate method was first proposed by Lucas *et al.* [20] to compute the creep exponent of indium. The method consists of loading at different strain rate and to measure the hardness using the Continuous Stiffness Measurement (CSM).
- In the hold load method the load is maintained constant and the strain rate is measured as a function of the contact pressure according to equation (4) [21].

In this work, in order to determine this mechanical characteristic we have used different methods and observed that the hold load method is the more reliable one. The principle of the method consists of applying a constant load

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after loading and computed the indentation depth rate/depth ratio as a function of the contact pressure. According to equation (4), the log-log plot of this two data should give a linear curve with a slope equal to the creep exponent. This method was first reported by Mayo *et al.* [22].

According to the literature, it appears that the value of the creep exponent with a hold load stage could be determined by this way. For example, Asif and Pethica [21] obtained a good correlation between experiments and the available literature for indium (n= 7.6). Raman and Berriche [23] compute the value of the creep exponent for tin (6.7-8.1), whereas Goodall and Clyne [24], using the same approach conclude that it is not possible to measure the creep exponent for materials like aluminum and magnesium.

During this study, we observe that it was not possible to obtain a reliable value of the creep exponent with only one experiment: An important standard deviation was observed. In order to obtain a value of the creep exponent in good agreement to the bulk value measured by tensile and torsion test, it is necessary to compute the average value from at least ten experiments. The origin of this dispersion is considered in the next section.

To reduce this dispersion the sample is loading at constant loading rate/load ratio until an indentation depth equal to 10 µm. Seven different loading rate/load ratio from 0.005 to 0.5 are used in order to see if the value of the creep exponent is sturdy and does not depend of the loading and creep velocity. After the load stage, in order to measure the creep exponent, a hold load time of 600 s is applied (Fig. 2.). For each loading rate/load ratio, six indentation tests have been conducted.

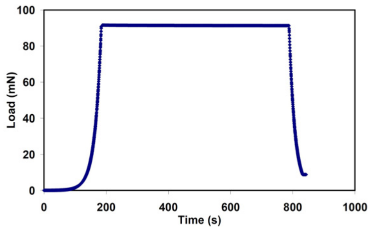

Figure 2: Typical load-time protocol used to calculate the creep exponent n.

3 Results and discussion

3.1 Elastic modulus

Fig. 3 shows the load-indentation curves for the three different protocols in the case of the indium quenched sample. During the hold load stage the penetration of the indenter is typically about 1 µm over 60 s. Indeed, indium exhibits significant creep that could be dramatic for the calculation of the elastic modulus. As shown in Fig. 4 a hysteresis is observed during the unload–reload stage. One can observe a Y shape: As accepted, for high loads, the stress is high enough to generate a continuous creep and the unload and reload curve are not similar. At the opposite, for low loads, the unload and reload curves are perfectly similar, one can conclude that the stress has enough decrease to became negligible: This parts of the two curves could be considered as reflecting a pure elastic behaviour and could be used to compute the elastic modulus according to the Oliver and Pharr method. The same observation could be done for all the unload-reload curves with the notable remark that the hysteresis is less marked with time. To confirm our hypothesis, we compute, the elastic modulus using i) the stiffness computed from the initial slope of the unloading curve (that is supposed to be influenced by creep) and ii) the stiffness computed from the initial slope of the reloading curve (that is supposed to not be influenced by creep) (Fig 4b).

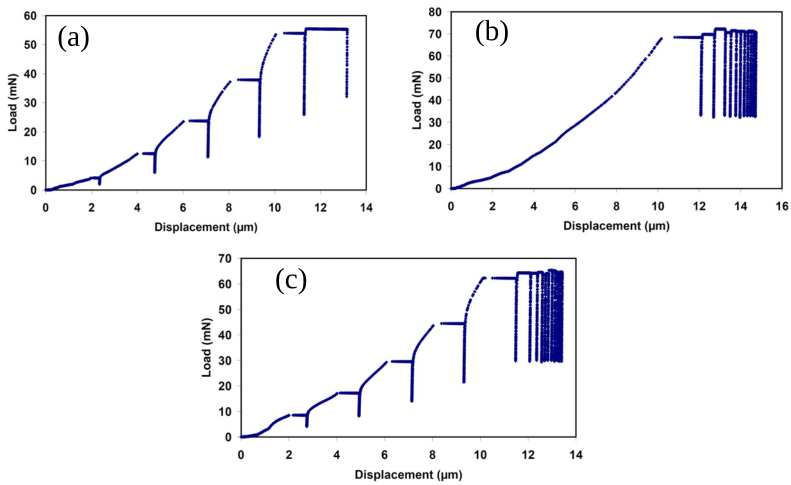

Figure 3: Load as a function of indentation depth in the case of indium quenched sample according to the three protocols: Cyclic unload-reload stage during load stage (a) hold load stage (b) load stage and hold load stages (c).

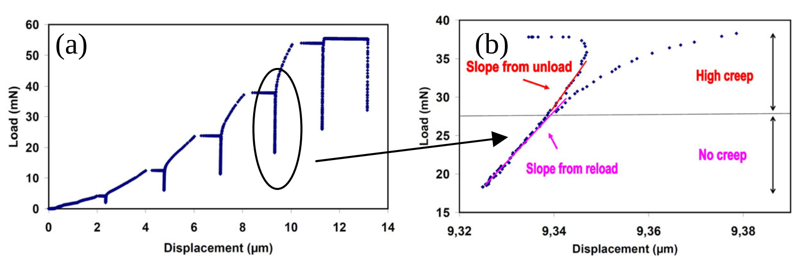

Figure 4: Load as a function of indentation depth (a) and zoom on a cyclic unload reload stage (b). One can see the hysteresis and the Y shape of the curve.

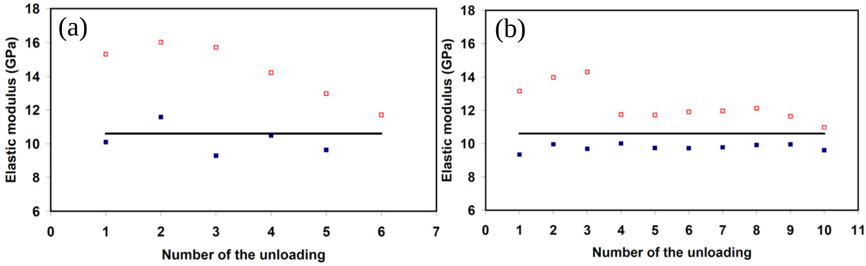

Figure 5: Elastic modulus for the indium quenched sample computed from unload (open points) and reload curves (solid points) for the different cyclic unload-reload stage during loading stage and protocol 1 (a) hold time stage and protocol 2 (b). The dark lines represent the elastic modulus calculated from a standard tensile test.

Fig. 5 shows that the values of the elastic modulus calculated from the unloading and reloading curves for different cyclic indentations. The dark line is the elastic modulus calculated from the standard tensile test (10.8 GPa) [25]. One can observe that, there is an important difference between the values of the elastic modulus computed from the unloading and the reloading curve. The values from the reloading curves are approximately equal to the value obtained from tensile test.

Whatever the protocol (Figs 5 and 6), we observe that the values computed from the reloading curves are approximately constant and accurate whereas the values computed from the unloading curves are no more constant and are typically 50% higher than the values obtained from the reloading curve and from tensile tests. As the number of cyclic indentation increases, the values computed from the unloading curves decrease and tend to the correct value as creep become negligible with time. This confirm that the beginning of the unload curve is influenced by creep even after a few minutes, and at the opposite the elastic modulus computed from the beginning of the reload curve is not influenced by creep whatever the loading and the creep history. Thus the method proposed in this paper is reliable and pertinent for the calculus of the elastic modulus in the case of visco-plastic materials.

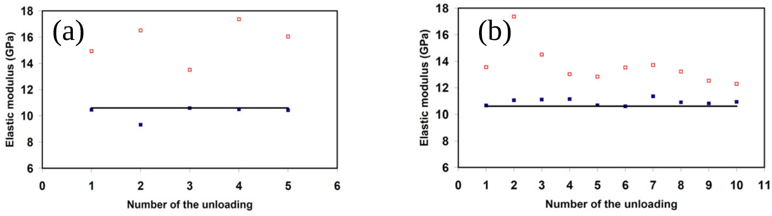

Figure 6: Elastic modulus for the indium quenched sample computed from unload (open points) and reload curves (solid points) for the different cyclic unload-reload stage during loading stage and protocol 3 (a) hold time stage and protocol 3 (b). The dark lines represent the elastic modulus calculated from a standard tensile test.

3.2 Creep exponent

In this section, we present the calculation of the creep exponent for indium and indium tin eutectic. For both materials, a quenched and annealed sample has been prepared. The data from the hold load stages are used to compute the strain rate and the contact pressure. The strain rate is equals to the contact depth rate/contact depth ratio (Equation (2)) and the contact pressure is given by the ratio of the load on the contact area (Equation (3)). Because, the materials have a very low hardness/elastic modulus ratio, we can make the approximation, thanks to the Oliver and Pharr model, that the contact depth is equal to the indentation depth.

Fig. 7 shows a logarithmic plot of the strain rate as a function of the contact pressure obtained for indium during hold load stage. Creep occurs during the hold load stage leading to a continuous decrease of the contact pressure and of the strain rate. The slope of the curve gives directly the creep exponent (Equation (4)). It has been observed that the curve is never a perfect straight line. Nevertheless, the creep exponent has been calculated using the linear portion of the curve on at least one decade of strain rate using the least square method.

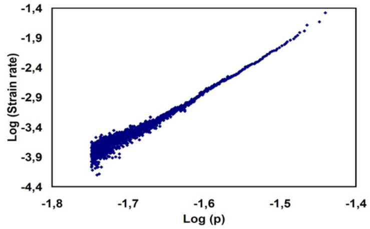

Figure 7: Logarithm of the strain rate as a function of the logarithm of the contact pressure (GPa).

Fig. 8 shows the values of the creep exponent for indium and indium tin eutectic as a function of the loading rate/load ratio during loading for the two thermal treatments previously described. The square in the figures represents the value of the creep exponent with the highest coefficient of determination and the dark lines represent the creep exponent for the indium (7.6) and indium tin eutectic (3.7) calculated from a tensile and shear test respectively [26, 27]. The error bars represents the lowest and highest values of the creep exponent from six experiments.

The above results clearly indicate that, with a hold load method, the creep exponent for indium and indium tin eutectic are approximately constant. Whatever the strain rates during loading, the creep exponent for indium and indium tin eutectic are approximately constant. It can be seen that reproducibility is poor especially for the quenched samples. Indeed, the value of the creep exponent for indium and indium tin eutectic is within the following ranges $5.4<n_{In}<12$ and $2.6<n_{In\text{-}Sn}<4.7$ for the quenched samples, and within the following range $5.1<n_{In}<9.1$ and $3<n_{In\text{-}Sn}<4.3$ for the annealed samples. Nevertheless, combining all the experiments, the average value and the standard

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deviation was found to be 7.51±1.45 and 3.70±0.40 for the indium and indium-tin eutectic respectively in good agreement with tensile and torsion values (7.6 and 3.7 respectively).

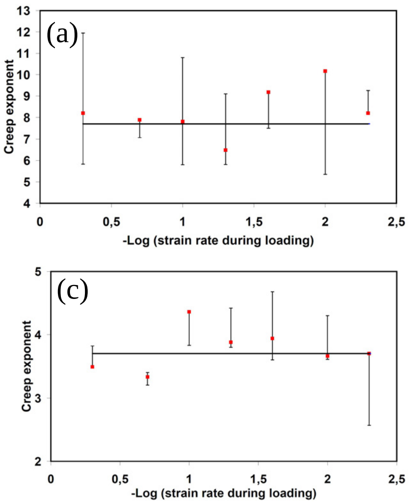

Figure 8: Creep exponent as a function of the strain rate (s^{-1}) during loading for indium (a,b), indium-tin eutectic (c,d), quenched (a,c) and annealed samples (b,d).

This dispersion should be related to the heterogeneity of the sample as the standard deviation is typically two times higher for the quenched samples. One can conclude that at the micrometer scale and for these two samples, the creep exponent is not constant. It is thus necessary to compute the average value of the creep exponent on sufficient number of experiment to obtain an accurate value.

4 Conclusion

An extended study has been realised to measure the elastic modulus and the creep exponent by nanoindentation for two viscoplastic materials, indium and indium-tin eutectic using cyclic indentation. The elastic modulus is computed using the Oliver and Pharr method and the contact stiffness computed from the beginning of the reloading curve to prevent the effect of creep. The creep exponent is computed from the power exponent of the strain rate-contact pressure curve during hold load plateaux. For the measurement of the creep exponent, it was necessary to realize a high number of experiments and compute the average value: The creep exponent was found to be highly dependent of the experiment, reflecting the heterogeneity of the creep behaviour at the local scale. As the opposite, the values of the elastic modulus were very similar whatever the experimental conditions. The values computed from these experiments are in very good agreement from tensile test for the both materials and the both thermal treatments.

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