

CONTINUOUS STIFFNESS MODE NANOINDENTATION RESPONSE OF POLY(METHYL METHACRYLATE) SURFACES

T. Iqbal^{a*}, B.J. Briscoe^b, S. Yasin^a and P.F. Luckham^b

^a Chemical Engineering Department, University of Engineering & Technology, KSK Campus, Lahore, Pakistan

^b Chemical Engineering Department, Imperial College, South Kensington, London, UK SW7 2AZ

Abstract Indentation is a comparatively simple and virtually nondestructive method of determining mechanical properties of material surfaces by means of an indenter inducing a localized deformation. The paper presents experimental results of the load-displacement curves, the hardness and the elastic modulus data, and associated analysis for poly(methyl methacrylate) (PMMA) surfaces as a function of contact displacement. The experimental results include continuous stiffness indentations performed using constant loading rate and constant displacement rate experiments. The continuous stiffness indentation involves continuous calculation of a material stiffness, and hence hardness and elastic modulus of surfaces, during discrete loading-unloading cycles, as in a conventional indentation routine, and in a comparatively smaller time constant. The dependence of the compliance curves, the hardness, the elastic modulus and the plasticity index upon the imposed penetration depth, the applied normal load and the deformation rate are described. Tip area and load frame calibrations for the continuous stiffness indentation are also reported. The paper includes practical considerations encountered during indentation of polymers specifically at low penetration depths. The experimental results show a peculiarly harder response of PMMA surfaces at the submicron (near to surface) layers.

Keywords: Nanoindentation; PMMA; Hardness; Modulus; Continuous stiffness.

INTRODUCTION

The evaluation of material mechanical properties at the submicron surface molecular layers has always been difficult. It is thought that these near to surface properties dictate some aspects of the contact performance of materials especially in many tribological and surface engineering applications. Consequently, material design and selection for these applications benefit from knowledge of such near surface properties. Indentation at the nanometric scale has been recognized as a means to probe the surface mechanical properties of materials at reduced penetration depths in the past two decades^[1–10].

The near to surface mechanical characterization by indentation is challenging. An indentation method which is based on optical imaging of the contact geometry, for example using an optical microscope, an electron microscope or an atomic force microscope, AFM, normal to the loading plane after indenter unloading is not suitable due to unavoidable and large errors for smaller penetrations. The inevitable presence of physical imperfections in indenter geometry is another problem encountered during the hardness determination by indentation^[1, 11, 12]. These indenter tip defects can be similar to the indent size and may cause a considerable inaccuracy in the property evaluations. These difficulties have been largely overcome using a continuous contact compliance method based on extent of the reaction force as a function of the imposed displacement, or vice versa, consequently giving a set of loading and unloading (compliance) curves for each indent. The elastic modulus and the hardness values are computed directly from the investigation of compliance curves obtained

* Corresponding author: Iqbal T., E-mail: t.iqbal07@imperial.ac.uk; tanveer@uet.edu.pk

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from the loading-unloading indentation cycles data. Hence, the experimental measurement of residual indent contact area is not needed in this method^[7, 13, 14].

Figure 1 shows a typical loading-unloading curve from an indentation cycle. The curve, also termed as a compliance curve, is a plot of normal load, P , as a function of indentation depth of the forced indenter penetration (displacement), h . Material properties prevailing the loading portion of the curve are the elastic modulus and the plastic yield stress. Precise nature of the unloading section is primarily governed by the elastic characteristics of material surfaces. In Fig. 1, $h_{\max}$ shows the maximum displacement of the indenter corresponding to the maximum normal applied load, $P_{\max}$, during the indentation cycle and h_r is the residual displacement resulting from deformation after the indenter is removed. Intercept of the tangent line, h_c , drawn from the initial part of the unloading curve at maximum load describes the elastic deformation effects^[7-9, 15, 16]. The slope of this line presents the contact compliance stiffness, S , evaluated at the maximum indentation displacement and h_c may be considered as being the actual value of the material displacement, which results mainly, but not solely^[7], in a plastic manner. Stiffness can be defined from simple geometric considerations as (Fig. 1),

$$S = \left(\frac{\partial P}{\partial h} \right)_{h_{\max}} \quad (1)$$

and

$$h_c = h_{\max} - \left(\frac{P}{\frac{\partial P}{\partial h}} \right)_{h_{\max}} = h_{\max} - \left(\frac{P}{S} \right)_{h_{\max}} \quad (2)$$

Analytic approach to the evaluation of the stiffness involves application of a power law to the unloading curve of the form

$$P = m(h - h_r)^n \quad (3)$$

where, m and n are fitting parameters. The parameter “ m ” depends upon the indenter geometry, sample Poisson’s ratio, sample elastic modulus, indenter elastic modulus and the final unloading displacement. The power law exponent “ n ” is related to the tip geometry of the indenter^[17, 18].

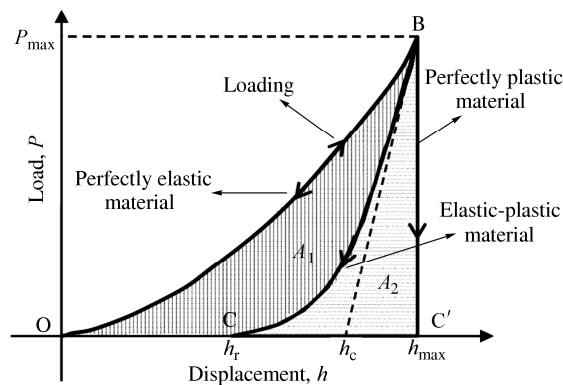


Fig. 1 Schematic of a typical indentation compliance curve (load-displacement data) for an elasto-plastic material (showing loading segment as OB and unloading segment as BC)

The area A_1 (OBC) represents the plastic work done while the area A_2 (CBC') is elastic recovery of a viscoelastic-plastic material. In case of purely plastic material, $A_2 = 0$, and the unloading curve is a straight line. For perfectly elastic material the unloading curve follows the same curve as loading curve resulting in 100% recovery.

There may be a considerable zero error uncertainty linked with the location of a loading origin point O (Fig. 1) in the load-displacement coordinates. The uncertainty can be minimized either by two ways; including a zero offset parameter, h_0 or by monitoring the contact stiffness variation during tip surface approach segment^[8,9].

The difference ($h_{\max} - h_c$) provides an estimation of the immediate elastic recovery of the material surface if an elastic response is assumed during the initial unloading^[7, 19]. To avoid errors resulting from the tip geometry of the indenter assuming as a flat punch, a correction factor, α , must be introduced, hence

$$h_c = h_{\max} - \alpha \frac{P_{\max}}{S|_{h_{\max}}} \quad (4)$$

where $\alpha = 0.75$ for a Berkovich tip indenter^[18]. The stiffness and the reduced elastic modulus relationship at maximum penetration depth for any indenter geometry is

$$S|_{h_{\max}} = \left(\frac{\partial P}{\partial h} \right)_{h_{\max}} = \frac{2\beta}{\sqrt{\pi}} E^* \sqrt{A_{\max}} \quad (5)$$

where $A_{\max}$ is the projected indentation contact area formed between the indenter and the material at $h_{\max}$, β is an indenter geometry dependent parameter ($1.026 < \beta < 1.085$)^[15] and E^* is the reduced elastic modulus of the contact. The reduced elastic modulus, E^* , is independent of the penetration depth and accounts for the Young's deformation of both the indenter and the sample, is defined as

$$E^* = \left(\frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_i^2}{E_i} \right)^{-1} \quad (6)$$

where E and ν with subscripts 's' and 'i' are the Young's modulus and the Poisson's ratios of the polymeric sample and the indenter respectively. The normal hardness is obtained as

$$H = \frac{P_{\max}}{A_{\max}} \quad (7)$$

The indentation response of polymeric materials in the unloading segment may demonstrate a creeping effect; that is, instantaneously after the unloading segment commences, the penetration depth increase to some extent, even though the imposed load reduces at a constant rate. This phenomenon, which may have arisen from the highly time-dependent relaxation and deformation characteristics of polymers, may significantly affect the estimation of the hardness of these surfaces (no elastic or viscoelastic recovery seems to occur at the initial unloading). This problem can be overcome by providing a specific hold segment at the peak load before consequent unloading^[4, 6].

The elucidation of the indentation of polymers creates further difficulties due to the complex viscoelastic-plastic response of these material surfaces plus their thermal sensitivity. Polymers demonstrate different behaviors under different contact situations caused by strain and strain-rate dependence of their characteristics. Consequently, the mechanical properties of polymeric surfaces are a function of the imposed contact conditions, such as the indenter geometry, the loading rate (*i.e.* strain rate), the penetration depth (the strain) and the ambient temperature. Our present work reports the surface mechanical properties of poly(methyl methacrylate), PMMA, using continuous stiffness mode indentation experiments. The experimental results include the load-displacement curves, the hardness, the elastic modulus and the plasticity index data and associated analysis for PMMA surfaces as a function of contact displacement.

EXPERIMENTAL

The Nanoindenter

The normal indentation hardness experiments were conducted on the polymeric surfaces using a nano-indenter system, Nano Indenter[®] II's machine, supplied by Nano Instruments Ltd., Tennessee, USA. A modified contact compliance mode indentation setup has been adopted with the machine. Hence, the machine has the capability to calculate both the elastic modulus and the hardness of a material surface being indented without actually determining the area of indentation. In contact compliance mode indentation the area is evaluated using depth of an indent and geometry of the indenter tip. The indenter tip geometry was determined by indenting against standard fused silica and then executing the indent area calibrations. The nanoindenter consists of three key structural components: an indenter column, an optical microscope and a precision Table.

The indenter column composed of a dual-tube assembly. The inner stainless steel tube was the load bearing element. The outer tube, made of a low thermal expansion coefficient iron-nickel alloy (INVAR), was coupled to the middle plate of the three plate displacement capacitor. Four leaf springs having high stiffness (10^4 N/m) in lateral and low stiffness (40–80 N/m) in vertical direction were connected to the outer tube. These springs were used to perceive an increase in load during surface detection operation and to steady motion of indenter shaft. The indenter tip, a trigonal pyramid tip housed at bottom of indenter column, known as a Berkovich Indenter makes an angle of 65.3° with the normal to the base^[9, 20]. An electromagnetic aluminium coil enclosed by a solenoid magnetic field was attached at the top of inner indenter tube. The appliance of voltage (–10 V to +10 V) to the coil produced the force to activate the indenter.

Continuous Stiffness Indentation

The continuous contact stiffness (dynamic mode) indentation based on the contact stiffness measurement during the loading segment of indentation was implemented in the present study as it offered several advantages for data acquisition. In this technique, the sample stiffness is calculated continuously during the discrete unloading cycles, as in conventional indentation routine, and in a comparatively smaller time constant (as can be seen in Fig. 2). The method offers a convenient way for measuring the contact stiffness and, hence, the hardness and the elastic modulus of indented surfaces at few nanometers of penetration and as a continuous function of the penetration displacement. The method is particularly useful in determining indentation properties of polymeric surfaces where creep is an important and restraining factor during the unloading segment and consequently after unloading^[21, 22].

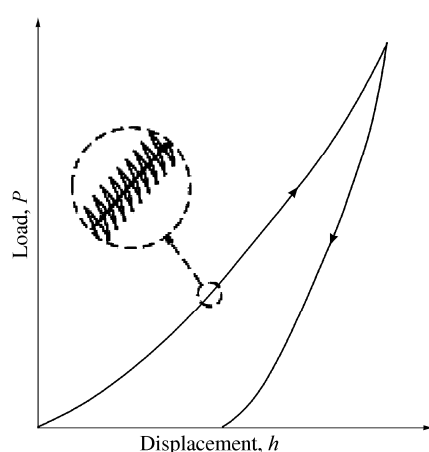


Fig. 2 Schematic of a typical compliance (load-displacement) curve of the continuous stiffness mode indentation loading-unloading cycle

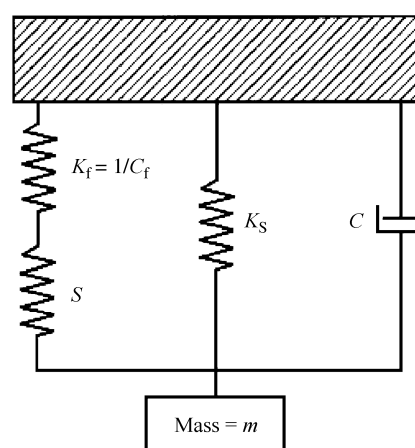


Fig. 3 Schematic representation of the dynamic model^[23]

An alternating current (AC), to impose a *ca.* 1 nm amplitude tip oscillations at a frequency of 45 Hz, is superimposed on the direct current (DC), which establishes the force on the indenter, during loading process in this technique. The AC current cause the indenter to oscillate with amplitude and a phase shift based on the stiffness of the material. A two phase lock-in amplifier evaluates the phase and the amplitude of the oscillations with that of the forced AC signal to work out the contact stiffness. The imposed displacement (a_0) and the driving force (F_0) for the AC signal and the relevant responses of the indenter are characterized in Eqs. (8) and (9)

$$F = F_0 e^{(i\omega t)} \quad (8)$$

$$a = a_0 e^{i(\omega t - \varphi)} \quad (9)$$

As is shown in Eqs. (8) and (9), the displacement oscillates at the identical frequency, ω , as that of the imposed force but lags by φ . The imposed amplitudes of the force and the displacement reaction ratio can be represented in the form of Eq. (10).

$$\frac{F_0}{a_0} = \sqrt{\omega^2 c^2 + (k - m\omega^2)^2} \quad (10)$$

And the phase angle (φ) is written as

$$\tan(\varphi) = \frac{\omega D}{(k - m\omega^2)} \quad (11)$$

where, c is the damping factor for the middle plate of the capacitor, m is the indenter mass and K is the spring constant of the system (shown in Fig. 3) in Eq. (12).

$$K = K_s + \frac{1}{\frac{1}{S} + \frac{1}{K_f}} \quad (12)$$

The above equations are solved to yield the contact stiffness, S , and the damping caused by the air gaps between the capacitor plates, ωC , as in Eqs. (13) and (14)^[11].

$$S = \left[\frac{1}{\frac{F_0}{h(\omega)} \cos \varphi - (K_s - m\omega^2)} - K_f^{-1} \right]^{-1} \quad (13)$$

$$\omega C = \frac{F_0}{a_0} \sin \varphi \quad (14)$$

Tip Area and Load Frame Calibration

The nanoindenter was calibrated for the so called tip area function, which illustrates the real area of indentation of the diamond tip indenter and load frame stiffness calibrations conducting indentation experiments on fused silica. The tip area function is significantly important to account for the unavoidable limitations in the tip geometry caused by the wearing during its life and the technological restrictions from the manufacturing processes. These limitations in the tip geometry cause major changes in the experimentally probed area and hence potentially considerable inaccuracy in the hardness and the elastic modulus computations. The measured indentation displacement, and hence the contact area, is a function of the load frame compliance of the indenter. The load frame compliance is comparatively more significant in the continuous stiffness mode, where the

stiffness is determined in lesser time constants. The standard continuous stiffness mode (as illustrated in Nano Indenter[®] IIs, Operating Manual Instructions) experiments were performed on the fused silica sample in load range 10 mN and load range 700 mN with effective constant strain rate of 0.025 s^{-1} . The data acquired from 20 indentation experiments were averaged and then were run through an iterative process for determination of the load frame stiffness. The iterative algorithm involves plotting total compliance as a function of the inverse of the square root of the indenter area based on perfect Berkovich Tip. The computation of load frame stiffness was derived from intercept values as the total compliance of the sample needs to be zero at infinite depth. The load frame stiffness of the presently used nanoindenter system was determined to be $7.05 \times 10^7 \text{ N/m}$.

The calculated load frame stiffness was used to acquire the hardness and the elastic modulus of the fused silica sample based on another iterative procedure for diamond area calibrations. The data gained was used to plot the experimental contact area as a function of the contact depth for the present system. The curve obtained was run through a curve fit based on the polynomial function as shown in Eq. (15).

$$A = 24.5h_c^2 + m_1h_c + m_2h_c^{1/2} + m_3h_c^{1/4} + m_4h_c^{1/8} + m_5h_c^{1/16} + m_6h_c^{1/32} + m_7h_c^{1/64} + m_8h_c^{1/128} \quad (15)$$

where, A is the area based on indentation displacement, h_c . An initial factor of 24.5 is used to account for the perfect Berkovich tip indenter. The coefficients in the Eq. (15), m_1 to m_8 reports for the imperfections in the tip geometry and were determined from the curve fit study of the contact area and the displacement data. Figure 4 presents the experimental data evaluated during calibration of the nanoindenter and the indenter tip area coefficients.

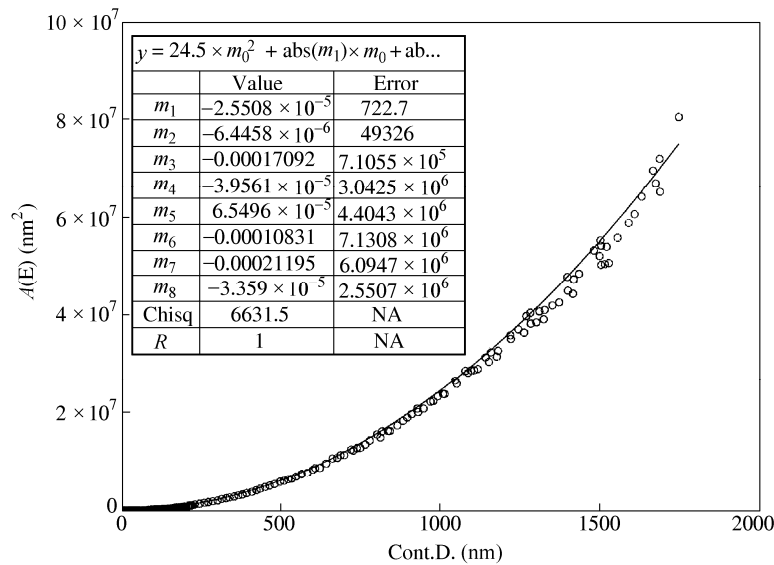


Fig. 4 Experimental contact area as a function of contact displacement for diamond tip area function calibration using indentation experiments performed on the fused silica

Materials

Commercially available poly(methylmethacrylate), PMMA (Catalogue # ME303013), was supplied by Goodfellow, UK. The average molecular weight of the PMMA samples was 495000. The amorphous PMMA surfaces were indented as received without any prior surface treatment. The average peak surface roughness of the polymeric samples was estimated using an optical profilometer and ranged between $0.1 \mu\text{m}$ and $0.5 \mu\text{m}$. Roughness of the surface that influences the experimental results is much less than that calculated by conventional profilometry.

Procedure

Continuous stiffness nanoindentation experiments were performed on amorphous PMMA surfaces at a constant loading rate *i.e.* 300 $\mu\text{N/s}$ to a maximum depth of 5000 nm and at constant displacement rate (5 nm/s) experiments as well. The indenter was held for 20 s at the maximum load to account for the material creep behavior of the polymer surface. A final hold segment of 50 s after 80% unloading was applied to account for the thermal drift during all indentation experiments.

RESULTS AND DISCUSSION

Load-Displacement (Compliance) Curves

Figures 5 and 6 show representative loading-unloading cycle data curves of the amorphous PMMA surfaces. The indents were spaced *ca.* 100 μm from each other. Figure 5 presents the compliance curves obtained following constant loading rate segments of 300 $\mu\text{N/s}$. The loading segment of an indentation cycle initiates from 0 nm indentation displacement to the maximum displacement of approximately 5000 nm. The maximum load was found to be (110 ± 5) mN for all the constant loading rate indentation curves. The indenter loading segment was followed by a load hold segment of 20 s at the maximum indenter load to account for the creeping effect^[4, 6]. The hold segment is needed to avoid nose formation during indentation process. The unloading step initiates from the maximum load to an unrecoverable depth at zero load of the polymeric surface. The unrecoverable depth is the plastic deformation of the polymeric material. The thermal drifts from the indentation experiment were accounted using a 50 s load hold segment after 80% load recovery in the unloading section.

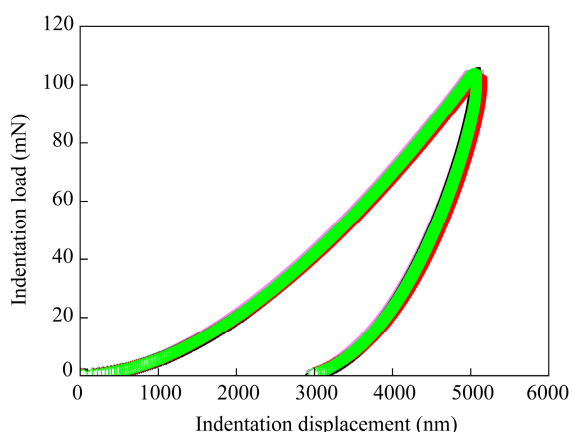


Fig. 5 Indentation load-displacement data for the as received PMMA sample at constant loading rate. The loading and unloading rates were maintained at 300 $\mu\text{N/s}$. The loading portion was followed by a hold segment (20 s) at the maximum indentation load. The compliance curves were obtained from the indents at 25 different locations of the virgin semicrystalline PMMA nominally 100 μm apart.

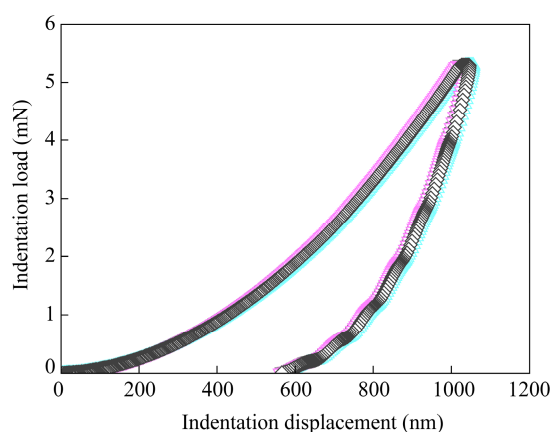


Fig. 6 Indentation load-displacement data for the as received PMMA sample at constant strain rate. The displacement rate was maintained at 5 nm s^{-1} during loading segment. The compliance curves were obtained from the indents at 25 different locations of the PMMA nominally 100 μm apart.

Figure 6 presents the compliance curves of the PMMA surface with a constant displacement rate 5 nm/s. The surfaces were indented to maximum penetration depth of 1000 nm followed by a hold segment to account for the material creep. Maximum indentation load for the constant displacement rate indentation is found to be (5.0 ± 0.5) mN. The plastic deformation or unrecovered indentation depth was found to be (550 ± 30) nm. The compliance curves for both constant loading rate and the constant displacement rate followed same trends and values for all the indents. The conformity of the curves indicates that the PMMA is a reasonable uniform and homogenous polymer. Briscoe and coworkers obtained the similar results following normal indentation without continuous stiffness mode for the PMMA surfaces^[2].

The normal response load was seen to remain negligible for all the indentation experiments at low indentation depths (approximately < 100 nm) during loading segment. This region is also called the induction phase of the indentation testing^[18] and may have occurred owing to the surface determination errors, the undeterminable physical defects of the indenter tip and associated uncertainties in the calibration procedures. The surface determination errors results from the surface roughness at nanometric scale of the surfaces. The precise range of the induction phase is inevitably unknown, therefore the load displacement data are presented as that obtained from the machine. The indenter to the material surface contact was established based on a doubling of the contact stiffness. A better insight can be gained from the subsequent data on the hardness and modulus. The tip area function and the contact stiffness of the indenter were calibrated, as described above, against a fused silica, which has a 10^2 to 10^4 times higher modulus than the polymeric surfaces, prior to indentation experiments on the polymers. The need for a standard material with Young's Modulus comparable to polymeric surfaces, for the stiffness and the tip area calibrations, is anticipated for the future. The authors tried to calibrate the indenter against a polystyrene surface based on its comparable nature to silica. But the calibration failed, the most probable cause may be the natural surface hardening of the polymeric material.

Hardness

Figures 7 and 8 shows typical indentation hardness data retrieved from continuous stiffness indentation experiments on the PMMA surface. The continuous stiffness mode experiments were performed on the surfaces at a frequency of 45 Hz with an amplitude of 1 nm during loading and unloading indentation cycles. The hardness values were determined using corrected indenter area function from fused silica calibrations and include zero error corrections. The typical uncertainty in values at lower penetration depth (< 100 nm) is not physically significant. These uncertain data points result from well recognized errors introduced by the deficiency in the procedures and applications to determine the tip geometry and the indentation size effects^[4, 23]. The figures show decreasing trends of indentation hardness for the amorphous polymer with increasing penetration depths. This might have resulted due to near surface modification/change in properties of the polymer due to manufacturing and/or physical aging. Briscoe and co-workers^[4] have also seen a similar response for amorphous polymers with normal indentation without continuous stiffness mode. The differences in decreasing trends can be attributed to the different scales of surface hardening for these polymers. An important factor to consider for comparing the data effect of hold segments on the properties of polymeric surface need to be considered for the indentation without continuous stiffness mode. Figure 7 shows the indentation hardness of the polymer as a function of indentation displacement for constant loading rate *i.e.* 300 $\mu\text{N/s}$. The induction period was found remain for an initial 50 nm and than a decreasing trend of the hardness to the maximum indentation depth *i.e.* 5000 nm. The hardness decreasing trend was seen to be less steep as penetration depth increases indicating more uniformity of the material at higher penetrations. The hardness values for the constant displacement rate loading segment (5 nm/s) are presented in Fig. 8. The computed average hardness values were found to be identical (*ca.* (0.3 ± 0.02) GPa) under two different experimental conditions. The hardness values were found to be fairly constant after the induction phase for the constant loading rate indentation. Although the average hardness values found from the two different experimental contact conditions were similar, both have shown different trends with increasing displacement. These differences can be attributed to the differences in contact conditions. The strain rate was higher in case of constant loading rate segment compared to the constant displacement rate segment. Hence the hardness values observed at lower strains are comparatively constant.

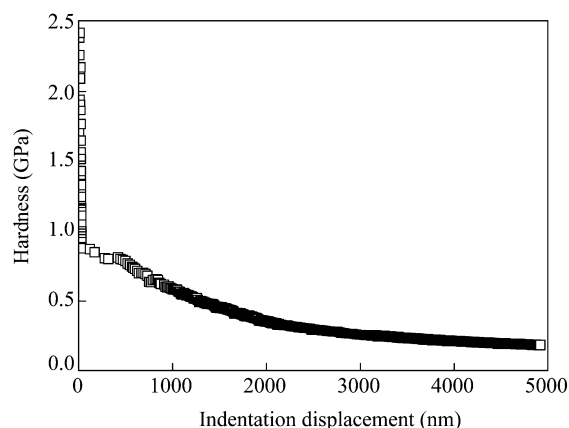


Fig. 7 Indentation hardness as a function of indentation displacement data for the as received PMMA sample at constant loading rate

The loading and unloading rates were maintained at 300 $\mu\text{N/s}$. The data were obtained from the indents of the polymer nominally 100 μm apart. (Data less than 300 nm may not be accurate due to surface approach and tip calibration factors.)

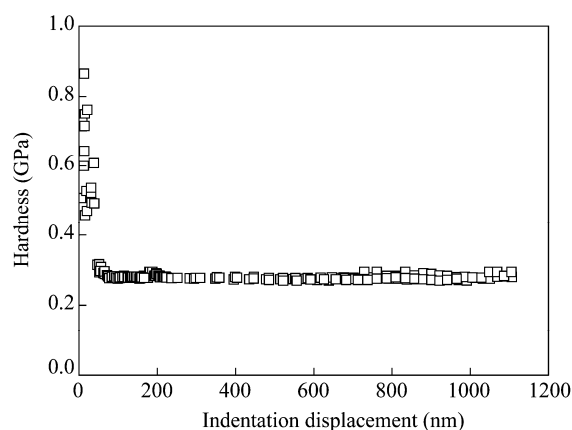


Fig. 8 Indentation hardness as a function of indentation displacement data for the as received PMMA sample at constant displacement rate

The displacement rate was maintained at 5 nm s^{-1} during loading segment. The data were obtained from the indents of the polymer nominally 100 μm apart. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)

Briscoe and Sebastian^[5] examined the indentation properties of the PMMA surfaces in the macro and micro scales; they reported the hardness values of 0.38 GPa in the mm range and 0.40 GPa in the micrometre range. The indentation experiments were conducted using a 90° conical indenter, under the controlled displacement rate. The fact that the hardness values reported in the present work are smaller than those values finds partial justification in the different experimental conditions followed for the two experiments. The present data is comparable to the hardness values reported by Briscoe and coworkers^[4] ((0.26 $\pm$ 0.05) GPa) using a Berkovich tip indenter but without continuous stiffness indentation. The modulus values calculated for the present work are comparatively partially higher than the modulus values reported elsewhere. These differences can be explained based on the differences in experimental conditions and the methods of data evaluations as explained above for the hardness values. Effects of hold segment on the properties of polymers need to be considered for comparing the indentation data with continuous stiffness and without continuous stiffness mode.

Elastic Modulus

The elastic modulus of the polymeric surfaces as a function of indentation displacement is represented in Figs. 9 and 10. The elastic modulus was calculated using Eq. (6). The reference elastic modulus (E_i) of the diamond Berkovich indenter was taken as 1141 GPa and the Poisson's ratio (ν_i) of 0.07. The Figures show uncertainties at lower penetration depths and this variation could be due to the same factors as discussed for the indentation hardness earlier. An increasing elastic modulus trend can be seen with decreasing penetration depth for the polymer which could find a possible explanation in localized modification of properties at polymeric surfaces. These modifications might be the result of exposure to light and air and/or fabrication processes. As discussed earlier, partially the uncertainty may also be from the indenter tip calibration errors. However, the trends from the two experimental contact conditions and also reported by others for polymeric surfaces are rather similar. Hence, if the inherent errors cannot be avoided, relative values of the modulus and the hardness can be used as reference for comparison purposes. The modulus values were comparatively constant for constant displacement rate loading indentation may be due to lower strain rate, whereas a continuous decreasing trend of the modulus can be seen for the constant loading rate indentation experiment. Although, the average hardness values were observed to be comparable (*ca.* (5.50 $\pm$ 0.05) GPa) from the two experimental conditions.

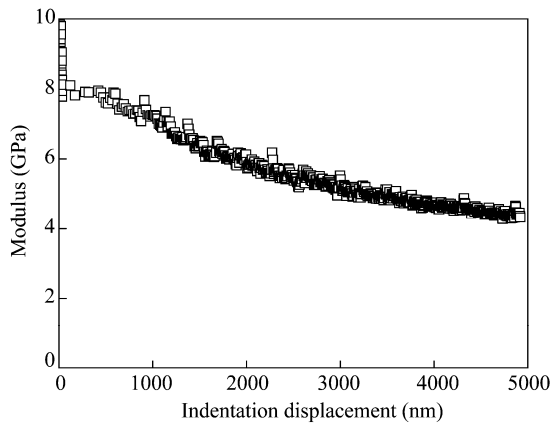


Fig. 9 Elastic modulus as a function of indentation displacement data for the as received PMMA sample at constant loading rate

The loading and unloading rates were maintained at 300 $\mu\text{N/s}$. The data were obtained from the indents of the polymer nominally 100 μm apart. (Data less than 300 nm may not be accurate due to surface approach and tip calibration factors.)

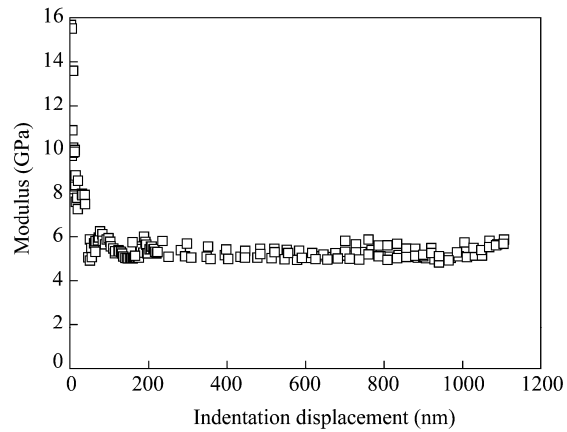


Fig. 10 Elastic modulus as a function of indentation displacement data for the as received PMMA sample at constant displacement rate

The displacement rate was maintained at 5 nm s^{-1} during loading segment. The data were obtained from the indents of the polymer nominally 100 μm apart. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)

Elasticity/Plasticity Analysis

The plasticity index was evaluated on the basis of relationship based on the hardness and the elastic modulus proposed by Mikić^[24] for perfect cones.

$$\psi = \tan \beta \frac{E}{H} \quad (16)$$

where, β is the angle of inclination of the indenter to the sample surface. The index is based on the relationship developed by Greenwood and Williamson^[25]. The original plasticity index values, in its most usually adopted form, contain the yield stress rather than the hardness term and the $\tan \beta$ term is raised to the half power. Since β , the angle of inclination of indenter, is constant for a Berkovich Tip indenter used in the present study therefore the ratio of elastic modulus to hardness as a function of indentation depth is presented for plasticity index. The hardness and the elastic modulus were evaluated from the continuous stiffness indentations mode as reported above for PMMA. This relationship has been discussed by Johnson^[26] and used by Briscoe and Sebastian^[2] for PMMA. Johnson^[27] tabulated the plasticity index values of different materials. The modulus to the hardness ratio was reported to be less than 10 for elastic materials. For perfect plastic material the ratio was seen to be more than 100. The intermediate values of the ratio represent the elastic-plastic response of the materials. Therefore, a material with higher values of the modulus to hardness ratio is more plastic. Figures 11 and 12 represent the plasticity index of the PMMA surfaces under different contact conditions. Figure 11 presents the plasticity index obtained using constant loading rate segment. The index value goes on increasing with increasing penetration depth indicating that the polymer behavior is more elastic at the surface. The plasticity index was found to remain within acceptable range of constant value when the polymer was indented using the constant displacement rate, as shown in Fig. 12. On the overall the index values were found to be greatly affected by the imposed contact conditions.

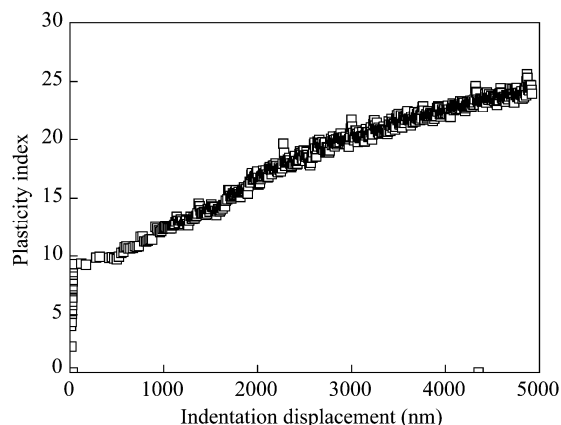


Fig. 11 Plasticity Index as a function of indentation displacement data for the as received PMMA sample at constant loading rate

The loading and unloading rates were maintained at 300 $\mu\text{N/s}$. The data were obtained from the indents of the polymer nominally 100 μm apart. (Data less than 300 nm may not be accurate due to surface approach and tip calibration factors.)

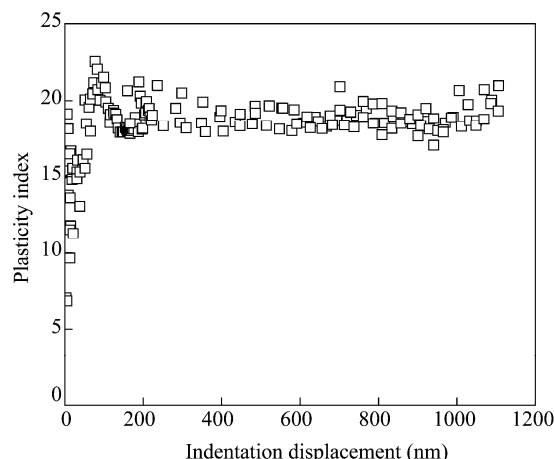


Fig. 12 Plasticity Index as a function of indentation displacement data for the as received PMMA sample at constant displacement rate

The displacement rate was maintained at 5 nm s^{-1} during loading segment. The data were obtained from the indents of the polymer nominally 100 μm apart. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)

CONCLUSIONS

The paper presents results of continuous stiffness mode normal indentation experiments performed upon poly(methylmethacrylate), PMMA surfaces at nanopenetration depths. The continuous stiffness indentation involves the continuous calculation of the material stiffness, and hence hardness and elastic modulus of surfaces, during the discrete loading-unloading cycles, as in conventional indentation routine, and in a comparatively smaller time constant. Experimental procedure and results for indenter tip and load frame calibrations are described along with practical limitations of the calibrations for polymeric surfaces. The load-displacement, the hardness, the elastic modulus and the plasticity index data are presented for constant loading rate and constant displacement rate experiments. PMMA is found to be a reasonably uniform and homogenous from the load-displacement curves. The surface mechanical properties of the polymer appear to increase at indentation depths closer to the surface. This might have resulted from the near surface modification/change in properties of the polymer due to manufacturing and/or physical aging. However, unestablished imperfections in the tip area calibration procedure may have contributed significantly to the near surface results. The experimental results are seen to be effected by the contact conditions. Finally, the continuous stiffness mode indentation appears to be a convenient method for estimating the surface mechanical properties of the polymeric surface.

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