

160 Method to account for edge and surface roughness effects in nanoindentation measurements of viscoelastic solids with a sharp tip

N. Fujisawa^{1a} and M. Łukomski¹

¹The Getty Conservation Institute, 1200 Getty Center Drive, Suite 700, Los Angeles, CA 90049, USA

^anfujisawa@getty.edu

Abstract. We have developed a method to address problems associated with the use of nanoindentation near the edge of a small object with a rough surface that can be applied to viscoelastic materials. To compare the performance of this method with the existing method that implicitly assumes the mean contact stress remains constant with penetration depth, both methods were applied to the dynamic indentation data of an acrylic-based paint thin film embedded in a resin of dissimilar mechanical properties. The existing method was shown to significantly overestimate the reduced elastic modulus of the material near the edge, whereas the present method correctly predicted the largely flat modulus profile across the film thickness. The method developed in this work enables detailed mechanical characterization of small and soft objects with inherently rough surfaces, frequently encountered in a wide variety of research fields including heritage conservation.

Introduction

The development of effective preservation methods for a work of art typically requires detailed mechanical and chemical analyses of its constituent materials performed in a minimally invasive manner. This obvious restriction imposes a strict limit on the volumes of original materials available for analysis, thereby ruling out conventional tensile and compression testing as viable options. Nanoindentation offers the possibility for direct mechanical characterization of a small volume of historic material, due to its ability to control the indent size at a nanometer resolution. In the case of a sample with a rough surface, however, the depth of indentation must increase to ~20 times the roughness depth to negate the surface roughness effect. Further, a deep indentation of a small sample would result in probing the combined response of the sample and its surrounding embedding material, rather than the intrinsic response of the sample itself. This work develops a method to extract the intrinsic mechanical properties of an embedded finite-volume sample with a rough surface from the indentation response.

Existing method

Where the frame compliance of the instrument is appropriately accounted for, the measured indenter displacement, h , at a given location on the sample surface consists of the local deformation of the sample due to indentation and the global deflection of the composite structure comprising its surrounding embedding material. It was shown that the effect of the latter can be modeled as the applied load, P , multiplied by a constant known as the structural compliance, C_s . Hence, the depth of penetration of the indenter into the sample, h^* , is conveniently given as [1,2]

$$h^* = h - C_s P. \quad (1)$$

If the elastic stiffness, S , is measured dynamically, the elastic stiffness due to indentation, S^* , is given by

$$1/S^* = 1/S - C_s. \quad (2)$$

Using Eqs. 1 and 2, the depth of the indenter in contact with the sample, h_c^* , is given as [2]

$$h_c^* = h - 0.75P/S - 0.25C_s P. \quad (3)$$

Therefore, if the value of C_s at a given test location is known, one can determine the compliance-corrected penetration depth, elastic stiffness, and contact depth thereof using Eqs. 1-3. There exists a method to determine C_s experimentally using the following correlation [1-3] derived from the Joslin-Oliver relation [4]:

$$\sqrt{P/S} = C_s \sqrt{P} + \sqrt{(\pi/4\beta^2)} \sqrt{H/E_r}, \quad (4)$$

where H is the mean contact pressure exerted by the indenter, E_r is the reduced elastic modulus of the sample with the indenter, and β is a geometric constant of the indenter that equals 1.034 for a Berkovich tip. The actual procedure involves plotting the experimental $\sqrt{P/S}$ versus \sqrt{P} and determining C_s as the slope of the scatter plot, assuming that $\sqrt{H/E_r}$ remains constant with penetration depth.

Novel method

While the assumption of constant E_r with penetration depth is reasonable for a viscoelastic material tested dynamically at a given frequency, the assumption of constant H with depth may become questionable when the indentation is performed in close proximity to the edge. In such a case, the material beneath the indenter is progressively over-constrained (or under-constrained) at increasing penetration depth by its surrounding

stiffer (or more compliant) embedding material. With this in mind, we propose a novel method of determining C_s that adapts the fundamental theory of indentation with a sharp tip by relating E_r to the ratio of elastic stiffness to contact depth [5]. Substitution of S^* and h_c^* to this theoretical relation yields

$$h - h_0 - 0.75P/S - 0.25C_sP = S/(2\beta \tan\theta E_r)/(1 - C_sS), \quad (5)$$

where h_0 is an effective contact point that defines the initial engagement of the indenter with a conceptual horizontal plane representing the base of a three-dimensional local surface height profile of the real sample, and θ is the effective cone semi-angle of the pyramidal indenter. This equation thus relates each of the three variables P , h and S to each other using three unknown constants h_0 , C_s and E_r . The novel method determines the effective contact point, h_0 , by extrapolating h to $P = 0$ using a regression model that describes the experimental h versus \sqrt{P} . The method finds a combination of the remaining two constants, C_s and E_r , that minimizes the sum of squares of the differences between the measured and model-predicted values of S using an iterative process implemented in Matlab® (MathWorks®).

Experimental

The material tested was a titanium white acrylic-based paint with pigment diameters of ~300 nm and a pigment volume concentration or PVC of 38 % (Golden Artist Colors, Inc.). A ~210- μ m thick paint film peeled from a Mylar® polyester sheet (on which it was casted) was embedded in a light-curing resin in paste form (Technovit® 2000 LC Fixierpaste, Kulzer GmbH) that exhibits a reduced modulus of ~15 GPa in fully cured condition. Through the use of an embedding paste rather than a liquid resin, the infiltration of this material into the paint sample was minimized. The embedded cross-section was dry-sanded by working through a sequence of grits from course to fine to realize a reasonably flat and smooth surface for indentation testing. A total of 34 indentations were performed across the entire thickness of the cross-sectional paint sample in a quasi-hexagonal array with a spacing of ~30 μ m. The narrowest distance between an indent and the sample edge was ~7 μ m. Two other pieces from the same paint film were mounted onto a rigid and smooth substrate using the same embedding resin paste – one sample was mounted top side up, while the second was underside up, allowing for indentation testing on both sides of the free film. All tests were conducted with a diamond Berkovich tip using the continuous stiffness measurement capability of the Ultra Nanoindentation Tester (Anton Paar) at an excitation frequency of 20 Hz. The quasi-static component of the load was increased exponentially with time to keep the strain rate constant at ~0.05 s⁻¹; hence, the mean contact stress remains constant at the beginning of the loading phase during which the edge effect is absent. The temperature in the test environment was ~20 °C while the relative humidity ranged from 41 to 50 %.

Results

The reduced elastic moduli of the top side and underside of the free film were determined from the mean slope of the elastic stiffness versus contact depth curve over the load range of 1.5 to 6 mN, with resulting values of 1.48 ± 0.07 GPa ($n = 9$) and 1.71 ± 0.05 GPa ($n = 9$), respectively. The indentation data for loads below 1.5 mN was excluded to negate a porous domain on the top side and a harder skin on the underside of the film, identified within a few microns below either surface.

All indentation data of the cross-sectional sample ($n = 34$) were analyzed using the novel and existing analysis methods in the load range up to 2.1 mN except for the single test performed closest to the edge, for which the load range was limited to ~0.85 mN to exclude the latter portion of its data reflecting the contact of the indenter with the resin surface. The existing method predicted a modulus increase to ~2.5 GPa towards either edge of the film, contradicting the results obtained on either side of the free film. In contrast, the novel method revealed a flat modulus profile across the film thickness with a baseline value of $1.64 \text{ GPa} \pm 0.18 \text{ GPa}$, commensurate with the modulus range of the free film. More importantly, the cross-sectional modulus analyzed by the novel method was found to correlate strongly ($R = 0.936$) with the mean contact pressure extrapolated to zero load. This indicates that the observed modulus scatter across the cross-sectional film was not due to the limitation of the method, but rather the reflection of the actual local properties of the sample comprising hard metal particles sparsely distributed (PVC of 38 %) in a random manner within a soft polymer matrix.

Conclusion

A method to overcome the issue of nanoindentation near the edge of a small and soft object with a rough surface was developed. Application of the method was successfully demonstrated for an acrylic-based paint thin film embedded in a resin. The method enables detailed mechanical characterization of small objects with rough surfaces, frequently encountered in a wide variety of research fields including heritage conservation.

References

- [1] J.E. Jakes, C.R. Frihart, J.F. Beecher, R.J. Moon and D.S. Stone: *J. Mater. Res.* Vol. 23 (2008), p. 1113-1127
- [2] J.E. Jakes and D.S. Stone: *Philos. Mag.* Vol. 91 (2011), p. 1387-1399
- [3] D.S. Stone, K.B. Yoder and W.D. Sproul: *J. Vac. Sci. Technol.* Vol. A 9 (1991), p. 2543-2547
- [4] D.L. Joslin and W.C. Oliver: *J. Mater. Res.* Vol. 5 (1990), p. 123-126
- [5] A.C. Fischer-Cripps: *Nanoindentation*, Publications/Springer, New York, NY (2011)