Nano-JKR Method Eliminates Adhesion Errors in Nanoindentation of Compliant Polymers and Hydrogels

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ABSTRACT

When indenting compliant polymers and hydrogels, adhesion between the tip and the sample leads to overestimation of modulus values when data are analyzed using the traditional Oliver-Pharr method implemented by most nanoindentation software. Instead of neglecting adhesion, the nano-JKR method analyzes the adhesive interaction between the tip and the sample using the Johnson-Kendall-Roberts adhesion model. This paper describes the nano-JKR method and reviews previous studies that have demonstrated its effectiveness for accurately measuring modulus values in compliant polymer and hydrogel samples with moduli between 50 kPa and 2 MPa. Implementation of the nano-JKR analysis method into commercial nanoindentation software packages would encourage more widespread adoption of this technique and improve the quality of data reported for nanoindentation of compliant materials.

Keywords: nanoindentation, adhesion, JKR, compliant

1 INTRODUCTION

Although nanoindentation (or instrumented indentation) was originally developed for characterization of hard, stiff materials such as metals and silicon, this tool has recently seen increased use with compliant polymers and hydrogels. One challenge associated with nanoindentation of these soft materials is adhesion [1]. Adhesion plays a more dominant role during indentation of compliant samples with blunt tips due to the increased indentation depths and contact sizes. Although commonly neglected, adhesion between the tip and the sample has been shown to lead to an overestimation of modulus values when data are analyzed using the traditional Oliver-Pharr method [2] implemented in most nanoindenter software [1,3-6].

The nano-JKR method was developed to address adhesion and accurately measure modulus values for soft materials using nanoindentation [3-5]. In the nano-JKR method, force curves that capture the entire adhesive interaction between the tip and the sample during tip approach, indentation, and tip retraction are collected using large diameter (≥200 micron) spherical tips and analyzed using a Johnson-Kendall-Roberts (JKR) contact mechanics model [7] that accounts for adhesion [3-5,8].

By accounting for adhesion rather than neglecting it, the nano-JKR method allows for more accurate modulus measurement in the presence of significant adhesion between the tip and the sample [3-5]. It also overcomes the challenges of tip sink-in during surface detection in compliant samples, which, when neglected, also leads to overestimation of modulus values [9]. However, because it is not implemented into nanoindentation software systems and requires off-line analysis of the data, the nano-JKR method has not been widely adopted and many researchers studying compliant materials using nanoindentation continue to use the inaccurate Oliver-Pharr method. This paper describes the nano-JKR method and reviews previous studies that have demonstrated its effectiveness for accurately measuring modulus values in compliant polymer and hydrogel samples to encourage broad adoption of this technique and future integration into existing nanoindenter software packages as an alternative to the Oliver-Pharr method.

2 NANO-JKR METHOD

To use the nano-JKR analysis method, full force curves need to be captured during data collection. Specifically, after the tip touches the surface, it is retracted before reapproaching the sample and performing the indent. This captures the entire adhesive interaction between the tip and the sample. A sample displacement-controlled load function is shown in Figure 1, and the resulting force curve is shown in Figure 2.

The unloading curve from force curves collected in this manner can then be analyzed using several different methods based on the JKR adhesion model equations, as described in detail by Ebenstein and Wahl [2]. The most rigorous approach is to fit the unloading curve load-displacement (P-δ) data with the following equation based on the JKR model equations:

$$\delta - \delta_{contact} = \frac{a_0^2}{R}\left(\frac{1+\sqrt{1-P/P_{adh}}}{2}\right)^{4/3} - \frac{2}{3}\frac{a_0^2}{R}\left(\frac{1+\sqrt{1-P/P_{adh}}}{2}\right)^{1/3} \quad (1)$$

where R, the radius of the indenter tip, is specified by the user, and the curve fit returns $\delta_{contact}$, a_o, and P_{adh}. $\delta_{contact}$ is a displacement offset variable that allows for identification of the effective point of initial contact between the tip and the sample, while a_o (the contact radius between the tip and the sample at P=0 during unloading) and P_{adh} (the pull-off force)

can be used to calculate the reduced modulus (E_r) of the sample using the following equation:

$$E_r = \frac{-3RP_{adh}}{a_0^3} \quad . \tag{2}$$

Figure 3 shows the curve fit results overlaid on the data used for curve-fitting for the Ecoflex 50 load-displacement curve shown in Figure 2.

A simplified analysis can be performed using only two data points from the unloading curve. These are labeled on the curve shown in Figure 2: the point where the load crosses zero (with displacement δ_0) and the point where the load reaches its minimum, also known as the pull-off force (with load P_{adh} and displacement δ_{adh}). Using these loads and displacements, the reduced modulus can be calculated from the following equation derived from the JKR model equations:

$$E_r = \frac{-3P_{adh}}{\sqrt{R}}\left[\frac{3(\delta_0 - \delta_{adh})}{1 + 4^{-2/3}}\right]^{-3/2} \quad . \tag{3}$$

For a full derivation of Equations (1)-(3), see Ebenstein and Wahl [3].

Both the curve fitting and the two-point method yield a reduced modulus, E_r, which is related to the elastic modulus of the material, E, by the following equation:

$$E_r = \frac{E}{(1-\nu^2)} + \frac{E_i}{\left(1-\nu_i^2\right)} \quad , \tag{4}$$

where E_i is the modulus of the indenter tip, and ν and ν_i are the Poisson's ratios of the sample and the indenter tip, respectively. When indenting very compliant samples with very stiff tips, as is the case in these experiments, the contribution of the indenter tip is negligible and Equation (4) reduces to:

$$E = (1-\nu^2)E_r \quad . \tag{5}$$

3 MATERIALS AND METHODS

Our previous studies used the nano-JKR method to characterize a variety of compliant silicone samples (Dow Corning Sylgard 184, Smooth-On Ecoflex 10 and 50, and Smooth-On Dragonskin 10 samples) and hydrogels (UV-cured polyethylene glycol (PEG) diacrylate) with nominal elastic moduli between 50 and 2000 kPa [3-5,8]. Silicone samples were prepared following manufacturer instructions and cast into molds to create 3 mm thick samples [5,8]. PEG (Aldrich, St. Louis, MO) hydrogels were prepared using the UV curing agent Irgacure 2959 (Ciba Specialty Chemicals, Tarrytown, NY), and cured under a UV lamp for 18 and 30 minutes for the 30% and 20% PEG gels, respectively, to create 2 mm thick samples [5].

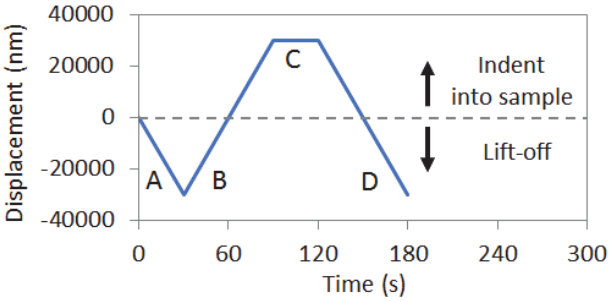

Figure 1: Sample displacement-controlled load function. Segment A represents the initial lift-off from the sample, segment B is the loading segment, segment C is the hold time at peak displacement, and D is the unloading segment.

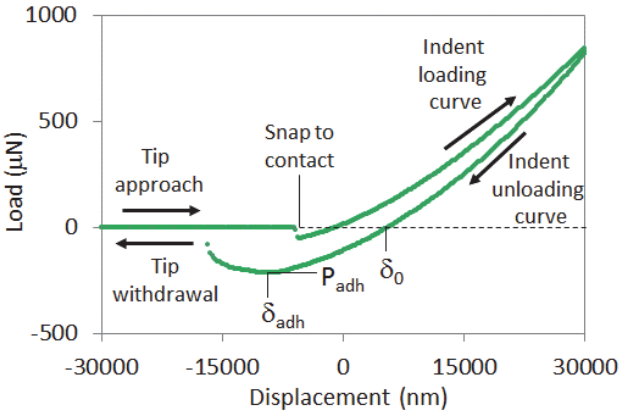

Figure 2: Representative load-displacement force curve for an indent in Ecoflex 50 using the displacement-controlled load function shown in Figure 1. The tip approach and loading curve map to Segment B in Figure 1, while the unloading curve and tip withdrawal map to Segment D. The load-displacement data from Segment A has been omitted for clarity. The data points used in the 2-point method are also labeled, including P_{adh}, the pull-off force or the minimum load recorded during pull-off, δ_{adh}, the displacement at pull-off, and δ_0, the displacement when the unloading curve crosses zero load.

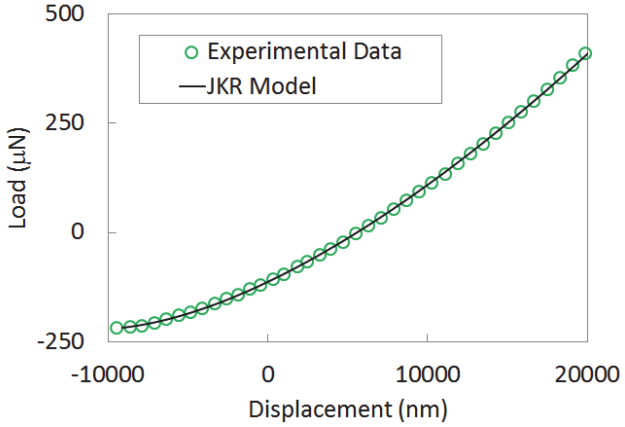

Figure 3: Sample curve fit results for the Ecoflex 50 indent shown in Figure 2. Experimental data from $-P_{adh}$ to $2*P_{adh}$, the data used to fit the JKR model, is shown here to demonstrate how well the JKR model fits the pull-off data.

Modulus values from nano-JKR analysis were validated by comparison with modulus values for the same materials measured using either unconfined compression [8] or nanoindentation in the presence of a surfactant [5], which eliminates adhesion and allows data analysis using the Oliver-Pharr method.

All indents were performed using a Hysitron TI-950 nanoindenter (Minneapolis, MN) equipped with an XZ-500 large displacement stage. All force curve indents were collected in displacement control using either a nominally 100 μm radius [5] or 400 μm radius [8] conospherical tip, as summarized in Table 1. The use of a large diameter conospherical tip to indent a low modulus, high surface energy material ensures that the data will be best analyzed using the JKR adhesion model (as opposed to the Derjaguin-Muller-Toporov (DMT) model, which is optimal for contacts involving stiff materials, smaller tip radii, and lower surface energy) [10]. This can be verified by calculation of the nondimensional Tabor parameter, μ [3].

Force curves were collected with displacement rates of 1000 nm/s and peak displacements of 10,000 nm for the Sylgard 184 samples [5] and 30,000 nm for the Ecoflex, Dragonskin, and PEG hydrogel samples [8], as summarized in Table 1. Hold periods ranged from 30 to 60 seconds depending on the sample type and were selected to ensure that creep would dissipate prior to unloading to allow measurement of an equilibrium modulus even when testing mildly viscoelastic materials. Lift-off heights also varied, ranging from 10 microns to 50 microns depending on how much height was needed for the tip to leave the adhesive interactive zone.

The displacement rate of 1000 nm/s was selected to be relatively slow, so that equilibrium behavior would be observed even when testing moderately viscoelastic materials. Although a previous study had determined that a displacement rate of 100 nm/s was optimal for Sylgard 184 samples to ensure equilibrium behavior [3], with the large lift-off heights needed in the reported studies, indent times would have exceeded 20 minutes per indent at 100 nm/s. Since there can be thermal drift during indentation, it is desirable to keep indent times as short as possible, so for the studies reported here a displacement rate of 1000 nm/s was used for all indents, keeping indent times under 5 minutes for all indents.

Data were analyzed by curve-fitting the load-displacment data from the unloading curve in the range of $-P_{adh}$ (the pull-off) to $2*P_{adh}$ using equation (1) as shown in Figure 3. MathCad (PTC, Needham, MA) was used for curve fitting and modulus calculation.

When converting from reduced moduli to the elastic moduli reported here, Poisson's ratios of 0.45 and 0.49 were used for silicone and hydrogel samples, repsectively.

4 RESULTS AND DISCUSSION

As shown in Table 1, a comparison of modulus results from different methods demonstrates that the nano-JKR method results in comparable moduli to other measurement techniques (within 10%). In contrast, analyzing the same force curve data using the Oliver-Pharr method leads to significant overestimation of the moduli for each material. This overestimation of modulus is typically larger for softer materials, for materials with higher surface energy (i.e., increased adhesion force), and for shallower indentation depths [5,6].

Table 1: Comparison of modulus values measured by validation methods (nanoindentation testing in a surfactant or unconfined compression testing) to modulus values measured by Oliver-Pharr analysis nano-JKR analysis of the same nanoindentation force curves [2,4]. Peak indent depths and tip radii used during data collection are also specified.

Material	Peak Indent Depth (μm)	Tip Radius (μm)	Validation Method	Oliver-Pharr Method		Nano-JKR Method	
			Mean Modulus (MPa)	Mean Modulus (MPa)	Percent Difference	Mean Modulus (MPa)	Pecent Difference
10:1 Sylgard 184 [4]*	10	100	1.640	1.759	7%	1.640	0%
20:1 Sylgard 184 [4]*	10	100	0.675	0.781	16%	0.682	1%
30:1 Sylgard 184 [4]*	10	100	0.216	0.280	30%	0.215	0%
Dragonskin 10 [6]	30	400	0.278	0.319	15%	0.268	-4%
Ecoflex 50 [6]	30	400	0.125	0.150	20%	0.121	-3%
Ecoflex 10 [6]	30	400	0.045	0.060	34%	0.046	4%
30% PEG Hydrogel [4]*	10	100	1.208	1.337	11%	1.292	7%
20% PEG Hydrogel [4]*	10	100	0.502	0.578	15%	0.540	8%

* Data were converted from reduced moduli reported in the original publication to elastic moduli to facilitate comparisons.

The depth and modulus dependence of errors due to adhesion is clearly illustrated in Figure 4. When indenting the 1.64 MPa 10:1 Sylgard 184 sample, the modulus was overestimated by 40% at 2000 nm, 11% at 6000 nm, and had reached an asymptote of 5% error by 20,000 nm. In contrast, for the more compliant 0.22 MPa 30:1 Sylgard 184 sample, the modulus was overestimated by 94% at 2000 nm, 40% at 6000 nm, and 12% and still decreasing at 30,000 nm. The high errors observed at lower displacements when adhesion is not accounted for are particularly significant when interpreting data in the literature because typical indent depths when indenting without a large displacement option like the XZ-500 stage tend to be less than 5000 nm.

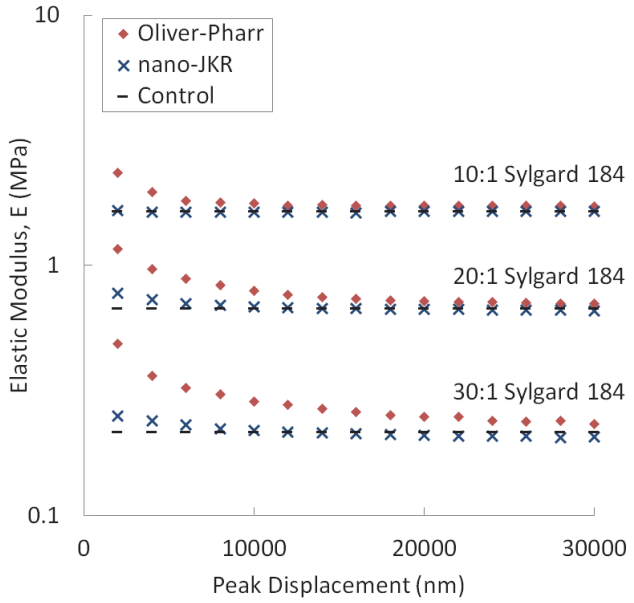

Figure 4: Modulus values for indents in 10:1, 20:1 and 30:1 Sylgard 184 silicone samples as a function of peak displacement. Indents in air, which exhibited substantial adhesion, were analyzed using both the default Oliver and Pharr method (Oliver-Pharr) which does not account for adhesion and the nano-JKR method (nano-JKR) which accounts for adhesion. The baseline control modulus, measured through nanoindentation of the same samples in a surfactant which eliminated adhesion, are shown for comparison (Control).

There are several challenges associated with using the nano-JKR technique. First, for the JKR analysis to be accurate, it is important for a truly spherical tip to be in contact with the sample; diamond tips cannot be ground to be perfectly spherical, so sapphire or glass tips are preferred. Second, as mentioned above, when testing compliant samples with high surface energy using a large diameter spherical tip, lift-off heights exceeding 50 microns may be required to fully remove the tip from the adhesive interaction zone before beginning sample approach. This can lead to large indent times, or could exceed the displacement range of the indenter. For this study, we used the XZ-500 large displacement stage to provide sufficient displacement range. However, in a previous study of silicone samples with moduli around 3 MPa, the same nano-JKR analysis was performed on force curves collected within the 10 μm limit of the same nanoindenter [3], demonstrating that it is possible to apply this method without the use of an extended displacement stage when testing less compliant or lower surface energy materials. Third, pull-off forces can sometimes be of such a high magnitude that they trigger the force overload of the indenter. Finally, because the data analysis method is not implemented in commercial software, data analysis requires off-line analysis, with more rigorous analysis requiring using either MathCad or another software program that accommodates non-linear curve fitting.

5 SUMMARY AND CONCLUSIONS

The nano-JKR method provides a practical method for calculating modulus values from nanoindentation analysis of compliant materials in the presence of adhesion. This technique would be equally applicable to analysis of indentation force curves collected using an atomic force microscope (AFM), which often show visible evidence of adhesion. The nano-JKR method would be easy to integrate into commercial software, as it can be implemented either using a curve-fitting algorithm or using the simplified "two-point method" that relies on only two data points from the unloading curve. Broad adoption of the nano-JKR method through integration into commercial nanoindentation and AFM software packages would improve the quality of nanoindentation data reported in the literature and would facilitate comparisons of results between different studies or different measurement techniques.

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