Key Engineering Materials Vols. 345-346 (2007) pp. 1129-1132
online at http://www.scientific.net

Characterization of Polymer Adhesion Through Modified JKR Theory and Instrumented Indentation Technique

Gyujei Lee[1,a], Sang-wook Park[1], Seung-Kyun Kang[1], Kug-hwan Kim[1], Jae-hwan Han[1], Kun-nyun Kim[2,b] and Dongil Kwon[1,c]

[1]School of Material Science and Engineering, Seoul National University, Seoul 151-742, Korea

[2]Nano Mechatronics Research Center, Korea Electronics Technology Institute, Seongnam, Korea

[a]jerome72@snu.ac.kr, [b]kimkn@keti.re.kr, [c]dongilk@snu.ac.kr

Keywords: IIT, JKR theory, PDMS, Polymeric stiffness, Work of adhesion.

Abstract. The Johnson-Kendall-Roberts (JKR) theory was combined with the instrumented indentation technique to evaluate the work of adhesion and modulus of an elastomeric polymer. An indentation test was used to obtain the load-displacement data for contacts between a diamond indenter and poly(dimethylsiloxane), PDMS. The JKR theory, modified to avoid the effect of ambiguous contact radius and depth for nanocontact, was applied to take into account surface adhesion and viscoelastic effects of the compliant polymer. Future work will include experimental verification that polymer stiffness in JKR contact is a time-dependent function.

Introduction

Polymer-based devices are playing an ever-increasing role in many areas of MEMS, displays (OTFT, OLED), and tissue engineering [1]. However, it is difficult to determine the mechanical properties of these compliant elastomeric polymers by general testing techniques because of their viscoelastic behavior [2]. The instrumented indentation technique (IIT) and its theory are well established for nano-mechanical characterization [3], but they have been validated only for elastic or elastoplastic materials with no surface adhesion effect, such as metals and ceramics. In order to take into account the surface force and viscoelastic effects in these polymers, many researchers have imported the Johnson-Kendall-Roberts (JKR) theory [4] into the IIT. This theory gives a solution for elastic modulus and work of adhesion as well as a relation between indentation load, depth, and contact area. The most readily applied algorithm for this theory, designed by Cho et al. [5], requires monitoring the contact radius optically through a transparent polymer specimen, and for nano-scale contacts of opaque polymers it is very difficult to measure the contact size optically. Many techniques using dynamic contact stiffness measurements [2] have been explored, but their complicated analysis algorithms and testing systems must be refined and simplified for in-field applications. In this study, a modified JKR theory will be combined with IIT to calculate the work of adhesion and material stiffness of PDMS, which is described as a function of unloading rate in order to verify the viscoelastic effect of the surface-force-dominated polymer.

Theoretical analysis

Work of adhesion. The contact mechanics of metals and ceramics for which surface adhesion can be neglected is based on Hertzian theory, but for compliant elastomeric polymers this theory underestimates the contact area and overestimates the modulus [4]. Surface-adhesion-dominated contact models have been developed in two extreme regimes that take into account the surface energy: the JKR theory (for high-surface-energy, compliant, elastic surfaces) and the DMT theory (for low-surface-energy, stiffer surfaces) [6] (see Fig. 1). The nondimensional Tabor parameter $\mu = \sqrt[3]{(R\Delta\gamma^2 / E_r^2 z_0^3)}$ is generally used to determine which model to apply (DMT for $\mu < 0.1$, JKR for $\mu > 5$, and a model transitional between the two between the limits) [7]. In the JKR analysis, the two governing equations are expressed by applied load P, relative depth from surface δ, real contact radius a, and work of adhesion $\Delta\gamma$:

$$a^3 = \frac{3R}{4E_r}\left[-P + 3\pi R\Delta\gamma + \sqrt{6\pi RP\Delta\gamma + (3\pi R\Delta\gamma)^2}\right] \quad \text{and} \quad \delta = \frac{a^2}{R}\left[1 - \frac{2}{3}\left(\frac{a_0}{a}\right)^{3/2}\right]. \tag{1}$$

To simplify these analyses, Pietrement and Troyon [8] developed a correlation between δ and P that is readily determined from the load-depth curve in the general instrumented indentation test. For the JKR analysis, $\alpha = 1$, $S_{(\alpha)} = 2/3$, and $\beta_{(\alpha)} = 1/2$:

$$\delta = \frac{a_0^2}{R}\left[\frac{\alpha + \sqrt{1 - P/P_{adh}}}{1+\alpha}\right]^{4/3} - S_{(\alpha)}\frac{a_0^2}{R}\left[\frac{\alpha + \sqrt{1 - P/P_{adh}}}{1+\alpha}\right]^{2\beta_{(\alpha)}/3} \tag{2}$$

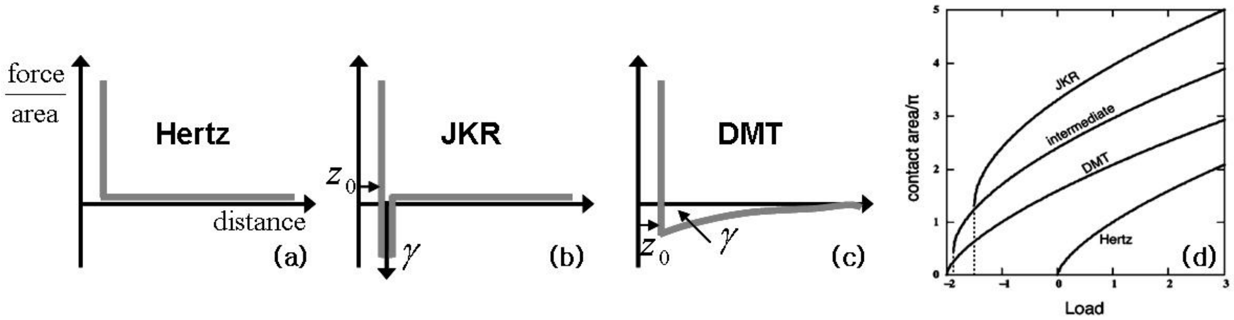

Fig. 1. Surface forces (per unit area) for (a) Hertz, (b) JKR, and (c) DMT models; (d) comparison of their contact area-load curve [4,6,7].

Stiffness and elastic modulus. In Hertzian contact (without surface adhesion), the normal stiffness, $S = dP/d\delta = 2E_r\sqrt{A_c/\pi}$, is a material constant related to contact area, while in JKR contact (with surface adhesion), material stiffness and modulus are time-dependent functions of the viscoelastic behavior. To remove ambiguities from the optical measurement of contact radius or depth, we can use the load-stiffness data relation as follows by partially differentiating Eq. 2 in terms of the depth δ:

$$\frac{a_0^2}{6R}\cdot\left(\frac{dP}{d\delta}\right) = \left(2f(P) - 1\right)\cdot\left(\frac{1}{3}f(P)^{-2/3} - 2f(P)^{1/3}\right)^{-1}, \quad f(P) = \frac{1 + \sqrt{1 - P/P_{adh}}}{2} \tag{3}$$

To describe the time-dependency of polymer stiffness, the unloading rate υ_u of indentation and viscosity v of polymer can be used as measurable variables:

$$S(\upsilon_u) = \left(\frac{dP}{d\delta}\right)_{P=P_{max}} = S_{max} + k\cdot\exp\left(-\frac{\upsilon_u}{v}\right) \tag{4}$$

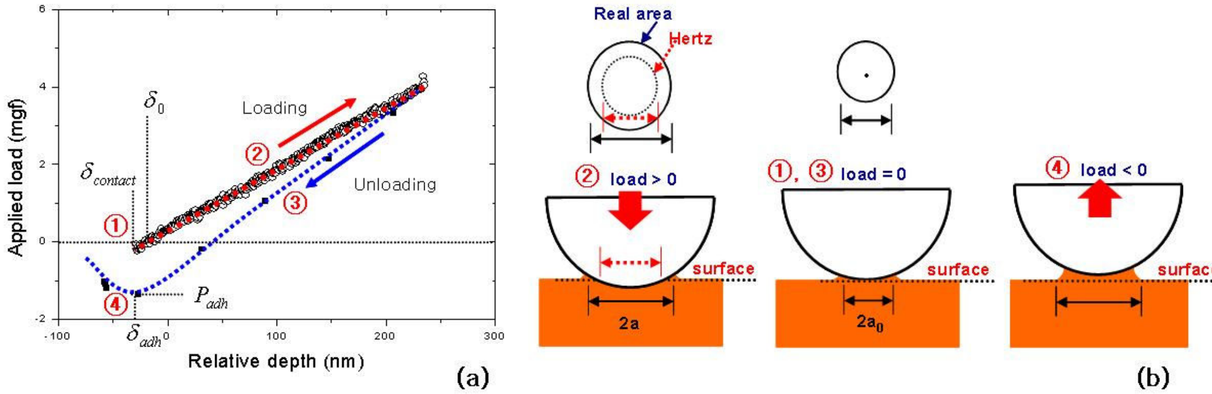

Fig. 2. (a) Applied load-depth curve showing surface energy and viscoelastic effect of compliant polymer (PDMS) and (b) schematic morphologies of contact area between tip and polymer surface.

Experimental details

Indentation was performed on the surface of a PDMS sample prepared as follows: a 10:1 ratio solution of siloxane monomer with crosslinking agent (Sylgard 184, Dow Corning, Midland, MI) was mixed, cast in a glass-surface mold, and cured for two weeks in a vacuum at room temperature. The reported properties of prepared samples were: $E_r \approx 3MPa$, $z_0 = 0.5\,nm$, $\Delta\gamma \approx 50-60\ mJ/m^2$ and $R = 100\,\mu m$, which established the JKR contact condition from the Tabor parameter $\mu \approx 603-683 \rangle\rangle 5$. Nanoindentation experiments were conducted using a TriboIndenter (Hysitron Inc., Minneapolis, MN) with 50 μN maximum load and five different unloading rates.

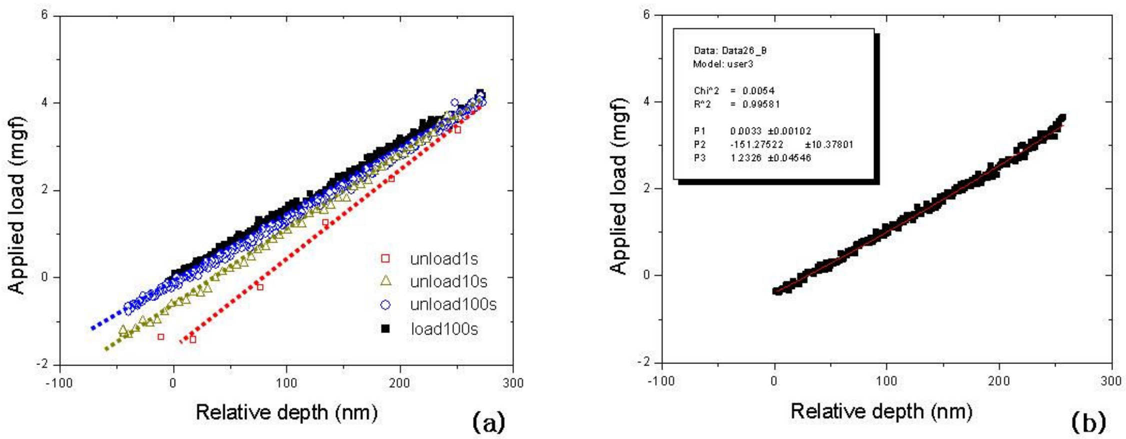

Fig. 3. Applied load-depth curve showing (a) unloading curves for PDMS for different unloading rates and (b) sampling curve-fitting process to obtain material stiffness in maximum load.

Results and discussion

The purpose of this study is to obtain the work of adhesion and modulus of elastomeric materials simply from readily measurable load-depth or load-stiffness curves by universal IIT, avoiding optical measurement of contact radius or depth ambiguities due to surface energy. Above we modified the existing JKR model into a correlation between maximum load and stiffness only, excluding the effect of contact radius or depth. In order to consider the time-dependency of polymer stiffness, we conducted simple experiments using nanoindentation on PDMS. Figure 2(a) shows a load-depth curve for PDMS at a relatively large unloading rate (50 $\mu N/\sec$). The viscoelastic behavior of PDMS is described from critical points such as contact depth $\delta_{contact}$ and maximum adhesion force P_{adh} . Figure 2(b) shows schematic morphologies of contact area underestimated by the adhesion-dominated nanocontact between the tip and polymer surface. To examine the viscoelastic stiffness of PDMS, we compared several unloading curves at different unloading rates, as shown in Fig. 3(a). We know that the informal stiffness ($dP/d\delta$, slope of unloading-depth curve) of PDMS increases with decreasing unloading time (or increasing unloading rate), a representative time-related variable. And we can calculate the unloading indentation stiffness using the unloading curve equation $P_{unload} = a\cdot(\delta-\delta_f)^m$ and its differential equation with contact depth δ by the sampling curve-fitting process shown in Fig. 3(b). The stiffness of PDMS, a viscoelastic material, was accurately described as a function of unloading rate (see Fig. 4(b)), unlike the constant normal stiffness of elastic or elastoplastic materials (see Fig. 4(a)). In particular, we see that the unloading indentation stiffness of PDMS converges to a specific stiffness value. According to those results, then, we can assume the following correlation function of polymeric stiffness with unloading rate and viscosity (or degree of polymerization): $dP/d\delta_{\max load} = S_{\max} + k\cdot\exp(-\upsilon_u/v)$, where $S_{\max}$ is a converging stiffness (perhaps dynamic stiffness-like properties), k is material constant, υ_u is unloading rate, and v is viscosity factor. We will perform nanoindentation experiments for various samples, peak loads and unloading rates in the near future in order to verify and refine the stiffness correlations in polymeric materials.

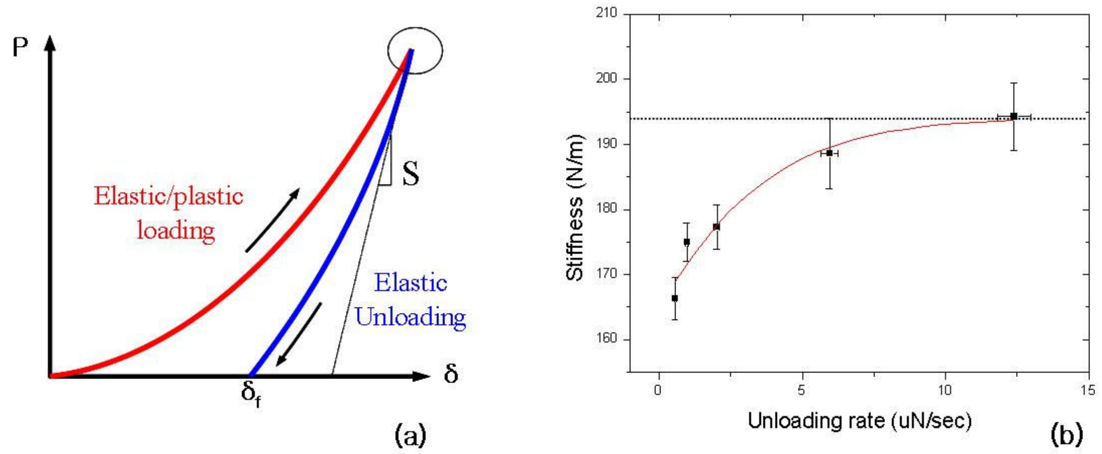

Fig. 4. (a) Constant normal stiffness of elastoplastic material and (b) time-dependent behavior of viscoelastic material (PDMS) where stiffness is described as a function of unloading rate.

Summary

In order to obtain the work of adhesion and modulus of compliant polymeric materials as simply as possible, we derived a modified JKR correlation with respect to load-stiffness curves that does not contain the ambiguous contact radius or depth. We clarified the time dependency of the unloading indentation stiffness in PDMS and developed a correlation of polymeric stiffness with unloading rate and viscosity.

Acknowledgments

This research was supported partly by a grant (2004-04392) from '*Center for Reliability Design Technology in Electronic Components*' under '*Specific Research Program'* of the Korea Science & Engineering Foundation, and partly by a grant (M102KN010009-06K-1401-00921) from '*Center for Nanoscale Mechatronics & Manufacturing*' under '*The 21st Century Frontier R&D Program*' of the Ministry of Science & Technology, Korea.

References

[1] K. Kim, Y.K. Kim, K.R. Lee et al.: J. Korean Sensors Soc., Vol. 15 (4) (2006), p. 277.

[2] D.M. Ebenstein and K.J. Wahl: J. Colloid Interface Sci., Vol. 298 (2006), p. 652.

[3] W.C. Oliver and G.M. Pharr: J. Mater. Res., Vol. 7 (1992), p. 1564.

[4] K.L. Johnson, K. Kendall and A.D. Roberts: Proc. Roy. Soc. London Ser. A. Math. Phys. Sci., Vol. 324 (1971), p. 301.

[5] K.W. Cho et al.: J. Adhesion Interface, Vol. 5 (3) (2004), p. 1.

[6] B.V. Derjaguin, V.M. Muller and Y.P. Toporov: J. Colloid Interface Sci., Vol. 53 (1975), p. 314.

[7] K.L. Johnson: Contact Mechanics, Cambridge Univ. Press, Cambridge (1985).

[8] O. Pietrement and M. Troyon: J. Colloid Interface Sci., Vol. 226 (2000), p. 166.