

Characterization of elastic modulus and work of adhesion in elastomeric polymers using microinstrumented indentation technique

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ABSTRACT

This study combines Johnson–Kendall–Roberts (JKR) theory with the instrumented indentation technique (IIT) to evaluate the work of adhesion and modulus of elastomeric polymers. Indentation testing was used to obtain load–displacement data for contact between a tungsten carbide indenter and the elastomeric polymer. The JKR contact model, which was designed to take polymer viscoelastic effects into account, was applied to adjust the contact area and the elastic modulus, which the Hertzian contact model would respectively underestimate and overestimate. In addition, we obtained the thermodynamic work of adhesion by considering the surface energy in this contact model. In order to define the relation between the JKR contact radius and applied load without measuring the contact radius optically, we used a relation between applied load and contact stiffness by examining the correlation between the JKR contact radius and stiffness through dimensional analysis with 14 elastomeric polymers. This work demonstrated that the interfacial work of adhesion and elastic modulus of a compliant polymer can be obtained from simple instrumented indentation testing without area measurement, and provided an algorithm for compliant polymer characterization.

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1. Introduction

The demand of the IT industry for higher speeds and capacities in information transmission and storage has rapidly made electronic parts smaller and thinner, and the thin-film structure of these parts produces more and more surfaces and interfaces. Consequently, adhesion reliability has become as important as the function of the thin films themselves. In addition, reliability-controlled design and development can lead to significant cost reductions [1]. Recently, the use of thin films, in particular elastomeric polymers, has increased in high-end electronics due to their many functional advantages, and early evaluation of adhesion reliability in such parts is much needed [2].

In many thin-film systems of metals or ceramics, the fracture-mechanical work of adhesion has been used to characterize adhesion because the fracture mode can be clearly observed. Elastomeric polymers, however, are very difficult to approach by fracture mechanics because they are very compliant and their fracture modes are difficult to define. Thus many researchers have adopted surface energy analysis to characterize the work of adhesion and other properties. Most of the many testing methods for

surface energy analysis are very complicated and not quantitative. One of the best methods, which is comparatively quantitative and easy to apply in the field, is Johnson–Kendall–Roberts (JKR) theory [3], which considers surface energy effects from the viewpoint of contact mechanics. There are, nevertheless, some restrictions in applying this method directly to general polymers. Here we combine JKR theory with instrumented indentation techniques to modify JKR theory using dimensional analysis and derive a new governing equation in terms of material stiffness.

2. Theory

2.1. Thermodynamic work of adhesion

Adhesion is the state in which two surfaces are held together by interfacial forces: valence forces or interlocking forces or both. Generally, adhesion has three components: basic, practical, and thermodynamic adhesion [4]. Basic adhesion is determined by the valence forces between atoms or molecules. Practical adhesion is defined as the work necessary to divide two joined materials into two parts, whether exactly along their interface or not. Practical adhesion is the combination of basic adhesion and other factors such as test method, temperature, residual stress, thickness, and material mechanical properties. Because these other factors are commingled with basic adhesion, quantifying basic adhesion in

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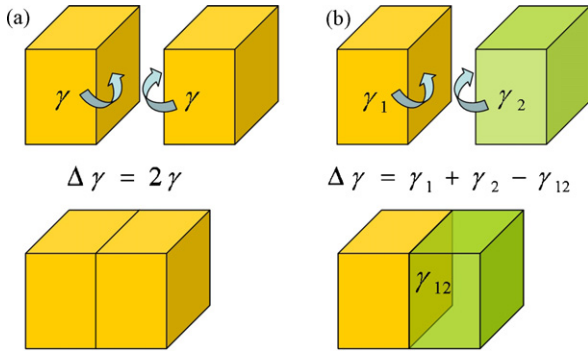


Fig. 1. Thermodynamic work of (a) cohesion: same material and (b) adhesion: dissimilar material.

a general adhesion test is very difficult. For that reason, considering the thermodynamic work of adhesion can be very useful in that its quantitative determination is relatively easy. The thermodynamic work of adhesion $\Delta\gamma$ is defined as the reversible work per unit area needed to generate the interface; see Fig. 1, where γ_1 and γ_2 are the surface free energies of material 1 and material 2 and γ_{12} is interfacial free energy generated newly when two materials are united. According to the above definitions, the thermodynamic work of adhesion is related to the material surface and interface energy, which can be derived from the contact angle. Here we usually measure the contact angle between a solid surface and a droplet dropped on it and use various models to derive the surface energy of the solid. However, this method yields different results depending on the modeling equations used, and in addition, specific reactions or interactions between the particular liquid and solid present cannot be excluded. In order to overcome these disadvantages and obtain the work of adhesion for elastomeric polymers with ambiguous or difficult-to-define fracture modes, the thermodynamic work of adhesion was analyzed on the basis of contact mechanics.

2.2. JKR theory and contact mechanics

According to the theory of contact mechanics, which began with Hertzian theory in the 1890s [5], the contact radius a is a function of the applied load P only when two perfect frictionless elastic bodies are in contact, as shown in Fig. 2(a):

$$a^3 = \frac{3RP}{4E_r}, \quad (1)$$

$$\frac{1}{E_r} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2}, \quad (2)$$

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}, \quad (3)$$

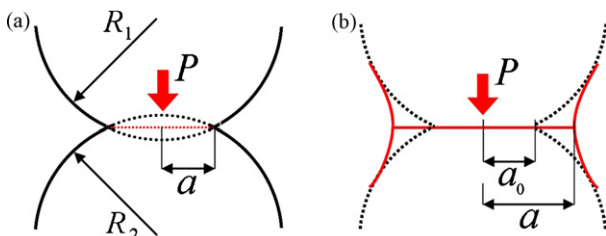


Fig. 2. Contact of two elastic bodies (radius R_1 , R_2) with applied load P and contact radius a in (a) the Hertz model and (b) the JKR model.

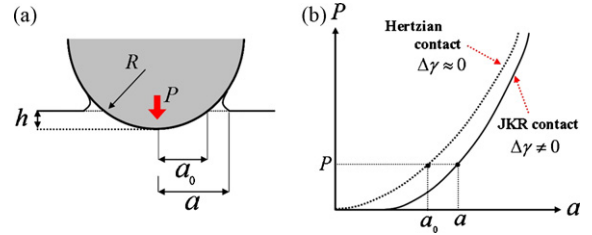


Fig. 3. Contact between a rigid hemispheric indenter and a flat compliant elastic polymer.

where R_1 and R_2 are the radii of the two curved surfaces, R is the relative radius, E_1 and E_2 are the modulus of the two materials, E_r is the reduced modulus, and ν_1 and ν_2 are Poisson's ratio of the two materials. This theory was developed and validated for elastic and elastoplastic materials such as metals and ceramics in which surface forces can be neglected. However, for surface-force-dominated materials such as compliant elastomeric polymers, this analysis underestimates the contact area (or radius) for the applied load P , as shown in Fig. 2(b). The intrinsic reason for these phenomenon is the thermodynamic work of adhesion, an interaction between the two surfaces that was newly considered in 1971 in the equation for Hertzian elastomeric contact by Johnson et al. [3]. Their equation is

$$a^3 = \frac{3R}{4E_r} \left[P + 3\pi R \Delta\gamma + \sqrt{6\pi R \Delta\gamma P + (3\pi R \Delta\gamma)^2} \right]. \quad (4)$$

When there is no work of intersurface adhesion ($\Delta\gamma=0$), Eq. (4) becomes the Hertzian Eq. (1). The key application of this equation is to obtain the work of adhesion and elastic modulus of elastomeric polymers if we can measure exactly the contact radius and applied load at that time. Accordingly, current JKR test systems using this algorithm usually have a micro-load cell to sense the contact load and a microscope to measure the contact radius. However, this means that the target specimen must be a transparent sphere (so that the contact area can be measured optically through this transparent specimen). In this study, we introduced surfaces of a hemispheric rigid body (indenter) and flat elastomeric polymer (target specimen) into contact as shown in Fig. 3, using an instrumented indentation system to obtain the contact area from applied load and contact depth without direct measurement of contact radius. We then designed an algorithm combining JKR theory and IIT (instrumented indentation technique).

3. Experimental details

3.1. Microinstrumented indentation test

In order to assess the contact load and depth exactly without optical measurement of the contact radius, we used an instrumented indentation system (Frontics, Inc., Korea) shown in Fig. 4(a). The instrumented indentation system measures and records contact load and depth continuously through indenter loading and unloading (see Fig. 5). The system specifications in this study are maximum load 10 N, load resolution 1 mN, and maximum displacement 300 μm . The indenter tip is a hemispheric rigid body of WC-Co (WC 89.4%, Co 10.0%, and others 0.60%) (see Table 1) and has various radii (250, 500, 1000, and 2000 μm); its mechanical properties are elastic modulus 6×10^5 MPa and Poisson's ratio 0.07, and the velocity of loading or unloading is fixed at 38.25 mN/s. We use a holding time of 30s between loading and unloading in order to exclude viscoelastic effects, and use 10-time

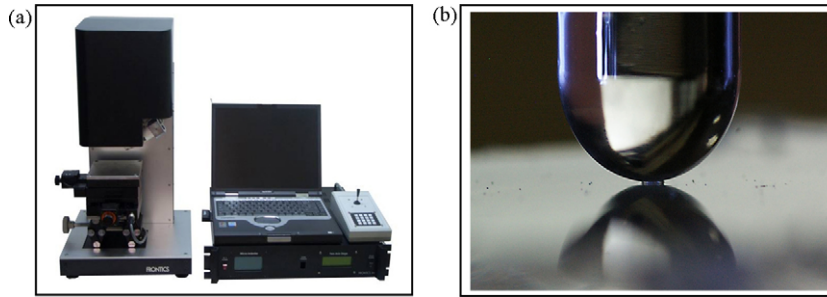


Fig. 4. (a) Microindentation system (Frontics, Inc., Korea) and (b) contact between indenter (WC-Co) and compliant polymer (PDMS).

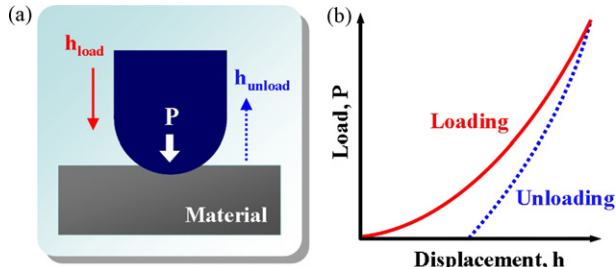


Fig. 5. (a) Instrumented indentation tester and (b) load–displacement curve in loading or unloading condition.

multiple indentation testing in order to obtain ten load–depth data.

3.2. Sample material

In order to verify our new algorithm, we prepared two materials: specimen 1 is PDMS (poly(dimethyl siloxane)) and specimen 2 is Si-RTV (silicon rubber), as shown in Table 1. For specimen 1, 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 in vacuum at room temperature for 2 weeks (see Fig. 4(b)). Specimen 2 was prepared by the same method using KE1606 (Shin-Etsu Chemicals, Japan). Surface-adhesion-dominated contact models have been developed for two extreme regimes that take surface energy into account: JKR theory (for high-surface-energy, compliant elastic surfaces) and DMT theory (for low-surface-energy, stiffer surfaces) [6] (see Fig. 6). 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 $\mu > 0.1$, and a model transitional between the two between the limits) [6]. The reported properties of prepared samples were: $E_r \approx 3$ MPa, $z_0 = 0.5$ nm, $\Delta\gamma \approx 50$ – 60 mJ/m² and $R \geq 100$ μ m, which established the JKR contact condition from the Tabor parameter $\mu \approx 603$ – $683 \gg 5$.

Table 1
Basic properties of PDMS and Si-RTV

Materials	Information	Elastic modulus (MPa)	Surface energy (mN/m)
Spherical rigid indenter			
WC-Co	WC 89.4%, Co 10.0%, others 0.50%	6×10^5	~ 0
Elastomeric polymer			
PDMS	Poly(dimethylsiloxane) weight ratio 10:1	1.04	22–25
Si-RTV	KE1606™ ~ confidential	<3.4	32

4. Results and discussion

4.1. Preliminary analysis

To use JKR theory in our characterization of compliant polymers, we had to verify that the elastomeric polymer has purely elastic behavior for the specified load and displacement using the microindentation system. We thus conducted preliminary experiments to confirm the purely elastic behavior of our specimen (see Fig. 7(a)) and to verify the repeatability and reproducibility of our system (see Fig. 7(b)). The commercially developed instrumented indentation system is usually designed to start measuring indenter displacement from the time when a microload cell registers the smallest load it can read. When surface adhesion is negligible, as in the contact of metal and ceramic surfaces, there is no depth-directional displacement when the indenter contacts the target material surface with no applied load. Consequently, we recognize the measured depth itself as the real depth datum, with no need to index the zero-loading point. However, when surface adhesion is dominant; as in the contact of compliant polymer surfaces, there exists in practice a depth-directional displacement when the indenter contacts the surface of target material with no applied load, as seen in Fig. 3 above. For this reason, the load–depth curve obtained from instrumented indentation systems (Fig. 8(b)) is distorted compared to the actual load–depth curve (see Fig. 8(a)), since the extent of depth-directional displacement is not considered due to the intrinsic character of these systems in the initial loading area.

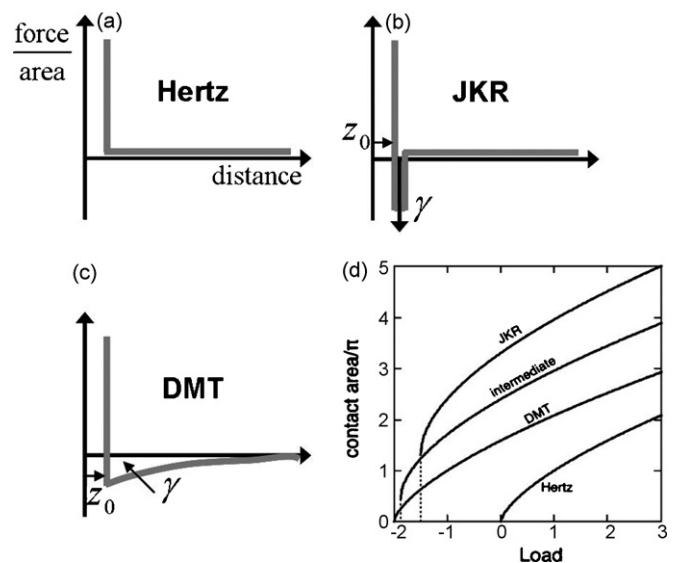


Fig. 6. Surface force per unit area with distance between two surfaces for (a) Hertz, (b) JKR, and (c) DMT models; (d) comparison of contact area–load curve [6,7].

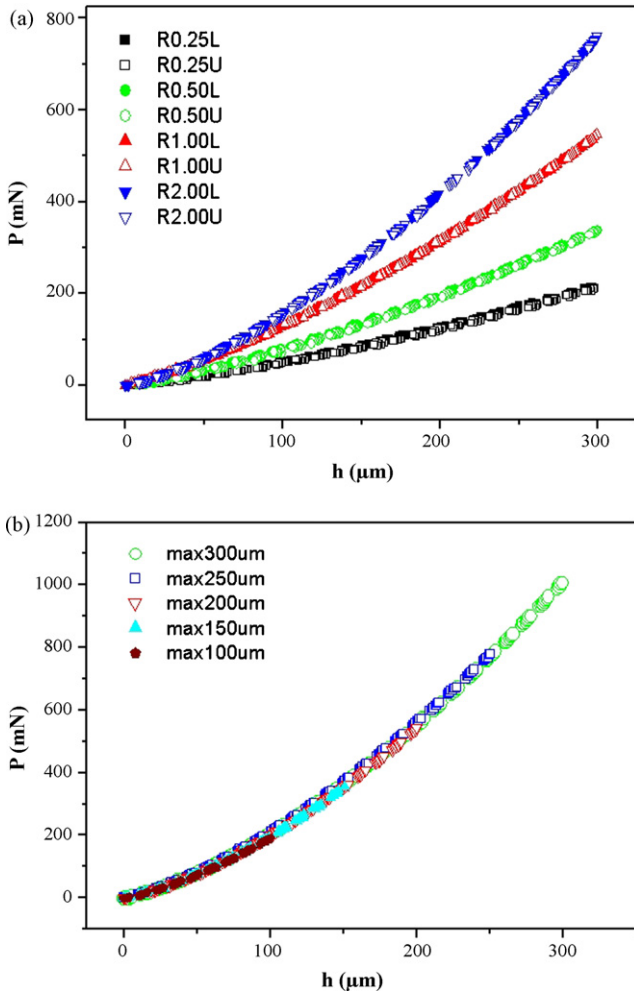


Fig. 7. Verification of (a) elastic behavior of PDMS (10:1) in experimental range and (b) repeatability and reproducibility of microindentation system used in this study.

In other words, the contact radius (or depth) obtained from the instrumented system (Fig. 8(b)) is inevitably underestimated with respect to the actual JKR contact (Fig. 8(a)) at constant load, and this makes it physically unacceptable to combine JKR theory with the instrumented indentation technique. In spite of all these problems, however, we find that the material stiffness (dP/dh) in two cases, increasing loading rate with contact depth, has the same value at constant load. Using this fact, we can combine the instrumented indentation system with JKR theory modified by indirectly using material stiffness instead of contact depth (or radius). In order to do this, we examine the relationship between contact radius and material stiffness.

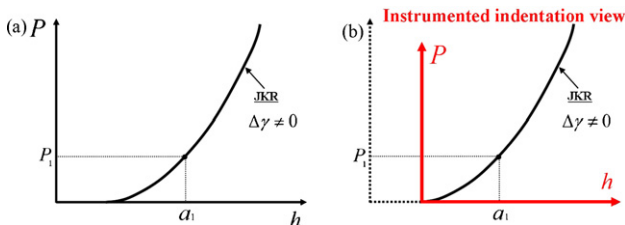


Fig. 8. Load-displacement curve of (a) real JKR contact and (b) distorted JKR contact from the viewpoint of a general instrumented indentation system.

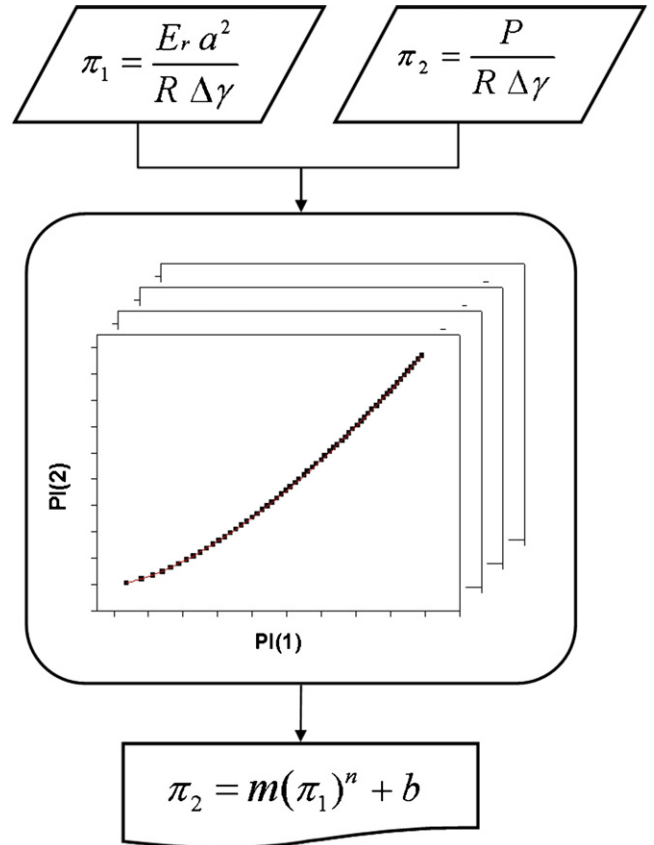


Fig. 9. Dimensionless parameters and schematic procedure for obtaining the correlation between two parameters through curve fitting.

4.2. Dimensional analysis

Dimensional analysis is a technique to reduce the number or complexity of the parameters affecting the specific physical phenomena. According to Buckingham’s PI theory (1914) [8], the number of dimensional parameters less the number of basic dimension is the same as the number of dimensionless parameters. The number of dimensional parameters in this JKR equation is five: contact radius (a), indenter radius (R), reduced modulus (E_r), work of surface adhesion ($\Delta\gamma$), and applied load (P); the number of basic dimensions is three: mass (M), length (L), and time (T). Therefore the number of dimensionless parameter generated in this case is two. The main variables, contact radius and applied load, can be distributed into dimensionless parameters, and by dimensional analysis (see Fig. 9) we can obtain two dimensionless parameters, π_1 and π_2 . In order to find the relation between these two parameters, we generated imaginary data through the JKR equation and the properties of 14 kinds of elastomeric polymer in terms of load and depth. For these data, we used curve fitting to find the correlation between π_1 and π_2 for each material as in the following power-law function:

$$\pi_2 = m(\pi_1)^n + b, \tag{5}$$

where the constants m , n , and b are coefficients and the exponent of dimensionless correlation obtained by curve fitting for each material; these constants have different values for each material. Substituting π_1 and π_2 into Eq. (5), we rearrange Eq. (5) by differentiating in terms of contact depth (h) and obtain the material

Table 2
Elastomeric polymers used in dimensional analysis and their K values and standard deviations [10]

Elastomeric polymers	K	S.D.
(A) PBLG	1.9215	0.0152
(B) PDMS	2.0170	0.0140
(C) PE(HDPE)	2.1819	0.0018
(D) PIB	2.0103	0.0153
(E) <i>cis</i> -PIP	2.0248	0.0147
(F) PMP	1.9905	0.0043
(G) PP	2.0469	0.0123
(H) PMDA	1.9639	0.0158
(I) PTFE	2.0670	0.0133
(J) PTHF	1.9768	0.0199
(K) PVAC	2.0248	0.0147
(L) PVA	1.9215	0.0152
(M) PVF	2.1819	0.0018
(N) PVDF	2.0670	0.0133

stiffness S as

$$S = \frac{dP}{dh} = KaE_r, \quad (6)$$

$$K = 2mn(\pi_1)^{n-1} \frac{da}{dh}, \quad (7)$$

where K is a coefficient generated in differentiation that contains the varying contact radius with contact depth (da/dh). In order to find the physical meaning of K , we refer to the elastic deformational equation of Bulychev [9] and infer from Eq. (8), modified by substitution of the formula for contact radius πa^2 for contact area A , that K can have constant value. Then, using the properties of the 14 materials previously prepared (see Table 2), we can calculate K for each material and find the result $K \approx 2$, as seen in Fig. 10:

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A} = 2aE_r. \quad (8)$$

Eq. (8) was derived analytically and verified through many experiments for the relation between contact radius and stiffness. Using Eq. (8), as confirmed in dimensional analysis, we modify the existing JKR Eq. (4) so as to obtain the thermodynamic work of adhesion and elastic modulus by the general indentation system without direct measurement of contact radius. After inserting the stiffness equation into the contact radius in the JKR equation, we express the applied load in terms of the stiffness as

$$P = \alpha(S^{1.5})^2 + \beta(S^{1.5}), \quad (9)$$

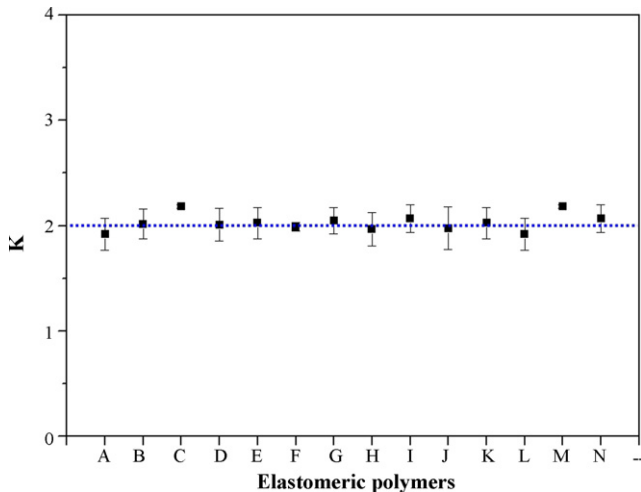


Fig. 10. Comparison of K values for different elastomeric polymers.

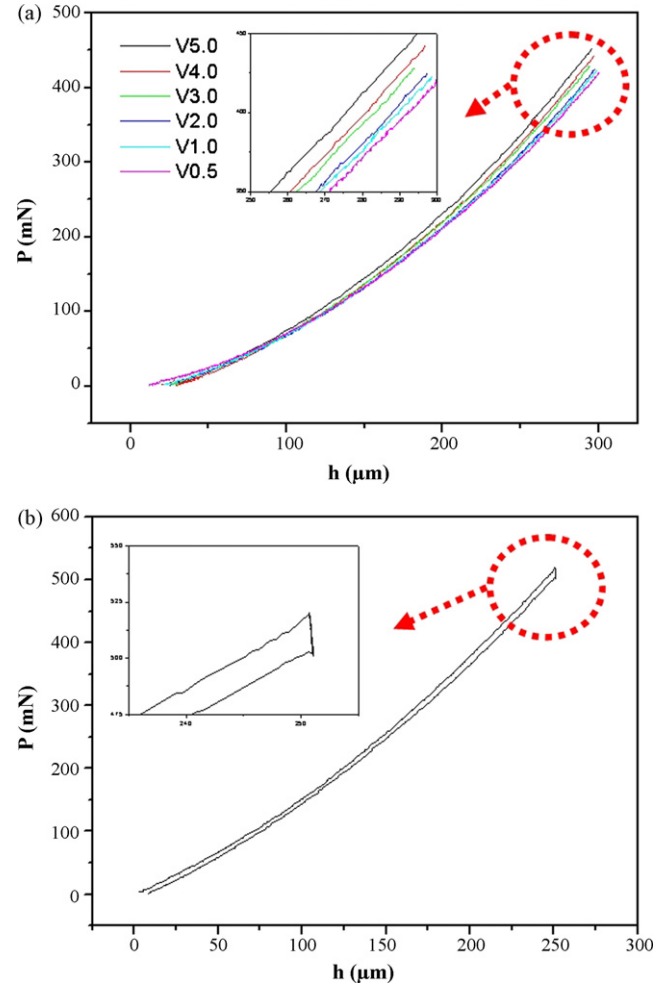


Fig. 11. Change in load–displacement curve with (a) increasing loading–unloading rate and (b) holding time (30 s) because of viscoelastic effects.

where the coefficients α and β are

$$\alpha = \frac{4}{3K^3RE_r^2}, \quad \beta = \sqrt{\frac{8\pi \Delta\gamma}{K^3E_r^2}}. \quad (10)$$

We can thus convert the load–depth data from the general indentation system into load–stiffness data that can be used in the newly modified JKR Eqs. (9) and (10); the target characterization of elastomeric polymers is made possible by α and β obtained by curve fitting of Eq. (9).

4.3. Exclusion of time-dependency

Appropriation of JKR theory for elastic contact analysis needs static indentation data that exclude the time dependency of elastomeric polymers. However, general indentation systems have intrinsic the time-dependent experimental conditions: loading or unloading rate and holding time (time between loading and unloading) that are revealed as viscoelastic effects of the compliant polymer. We can examine the effect of time dependency on the experimental results by simple experiments. Fig. 11(a) shows that load–depth data changes with loading or unloading rates. Fig. 11(b) shows that there is some difference between loading and unloading data when holding time is present. In order to find the holding time appropriate to exclude time dependency, we defined the load–decreasing rate as the decreasing rate from the maximum load in

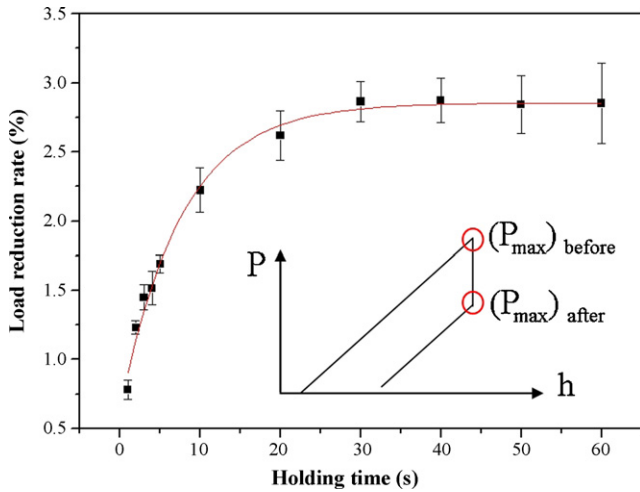


Fig. 12. Load-decreasing rate with different holding times and optimization of holding time.

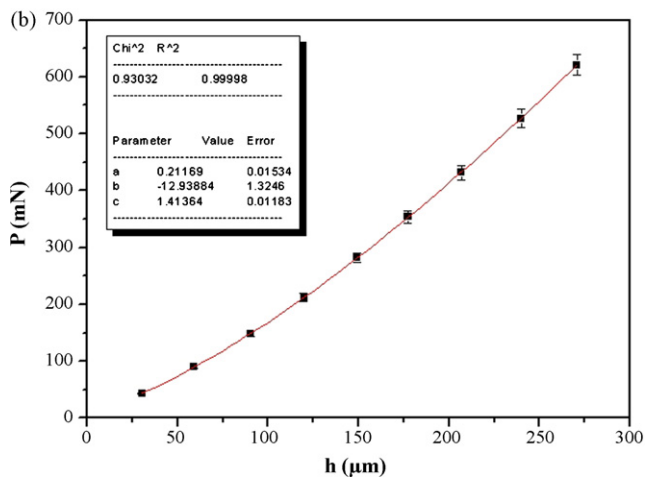
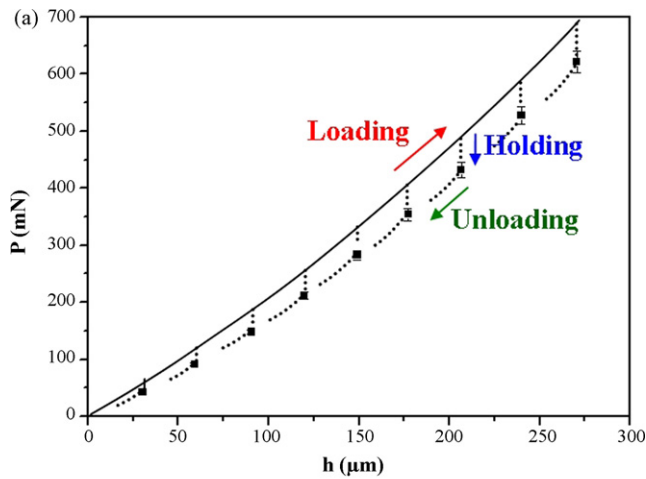


Fig. 13. Load-displacement data from 10 times repeated multiple indentation test: (a) excluding time dependency of polymeric materials and (b) curve fitting.

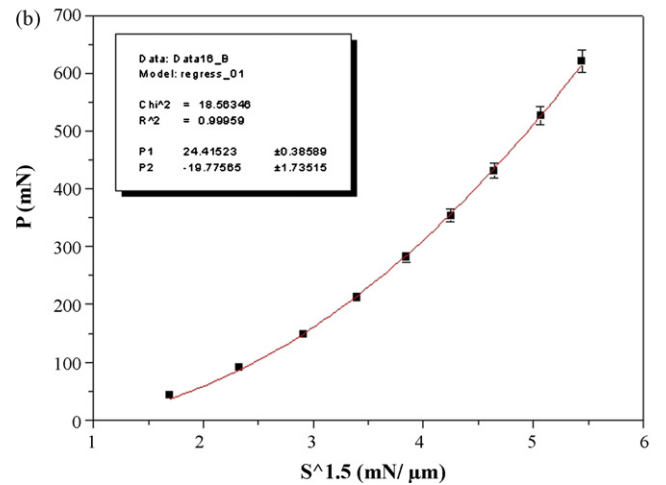
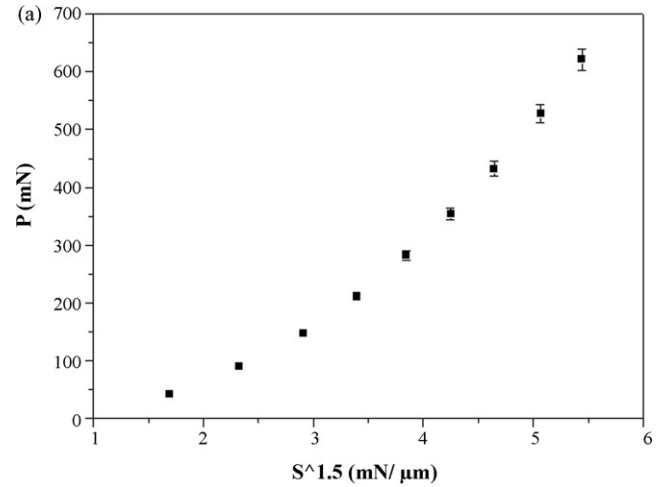


Fig. 14. (a) Load-stiffness data calculated from power-law fitting of load-displacement data and (b) curve fitting.

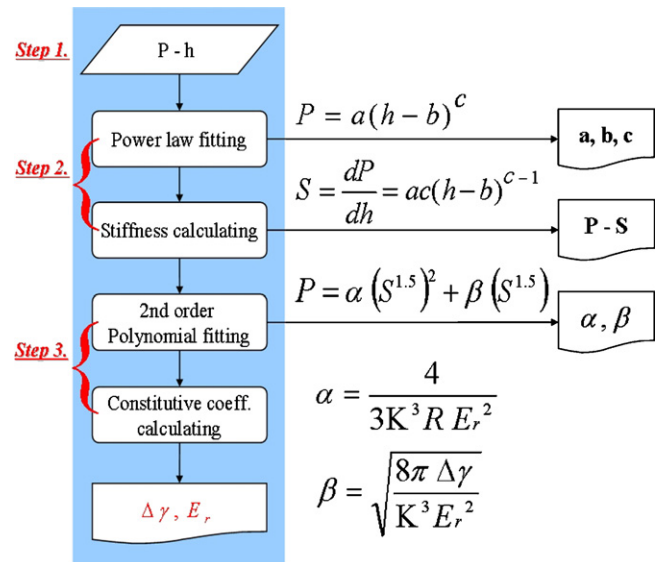


Fig. 15. Overall algorithm for mechanical characterization of elastomeric polymer using modified JKR theory and instrumented indentation system.

Table 3

Work of adhesion between indenter surface (WC) and elastomeric polymers (PDMS, Si-RTV), and elastic moduli of elastomeric polymers (PDMS, Si-RTV)

Materials	Work of adhesion (mN/m)		Materials	Elastic modulus (MPa)	
	Average	S.D.		Average	S.D.
PDMS + WC	39.63	18.03	PDMS	1.24	0.16
Si-RTV + WC	44.47	21.56	Si-RTV	2.17	0.30

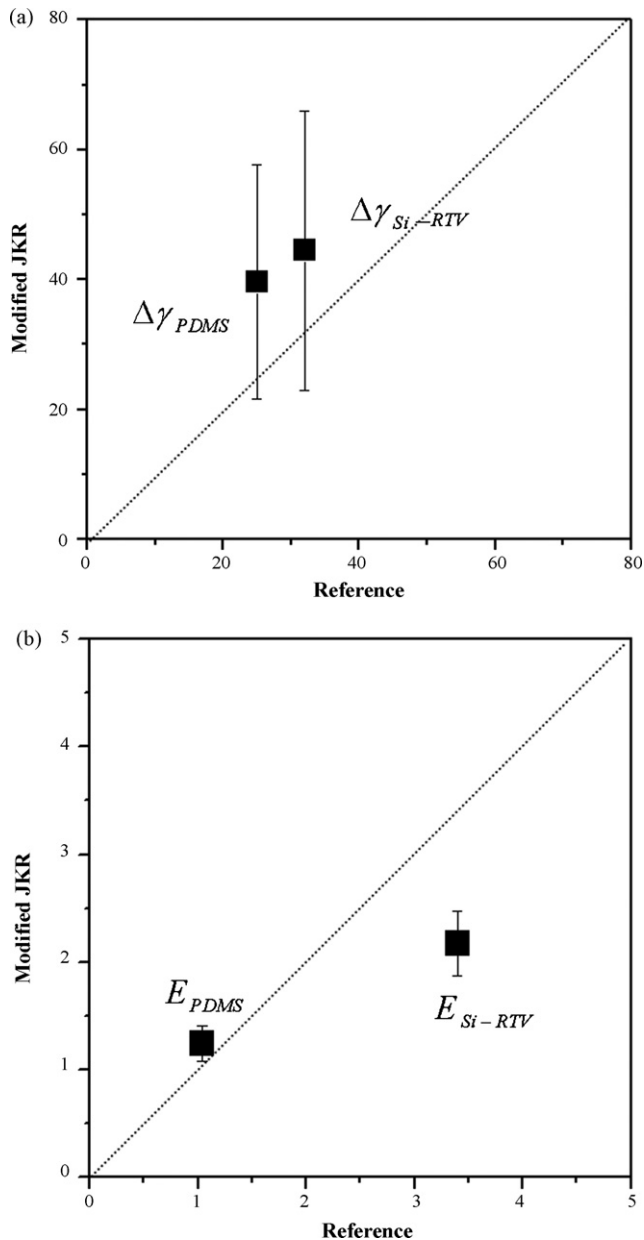


Fig. 16. Comparison of (a) work of adhesion and (b) elastic modulus from modified JKR theory and reference data [10].

loading to the minimum load in unloading and found that the load-reduction rate converges on some value after the available holding time, 30 s in this case (see Fig. 12). This initial experiment was reinforced as described below.

4.4. Overall algorithm

The newly modified JKR theory and the exclusion of time dependency described above let us construct the overall algorithm for characterizing an elastomeric polymer. The algorithm has three parts. Step 1 excludes instability due to polymer time dependency through the optimized holding-time setting in Fig. 13(a). Step 2 obtains the $P-h$ power-law function through curve fitting, as shown in Fig. 13(b), with the ten times multiple indentation method. In step 3, using the power-law function obtained above, $P-S$ data are obtained by simple differentiation (Fig. 14(a)), and finally we find the work of adhesion and elastic modulus from the modified JKR equation (Fig. 14(b)). All these processes have been rearranged into the stepped algorithm, as seen in Fig. 15.

5. Conclusion

JKR theory has been very useful in characterizing the work of adhesion and elastic modulus of elastomeric polymers, but it has the inevitable limitation that the contact radius must be measured directly by microscope; it is thus impossible to apply this method to opaque materials. We therefore combined the indentation technique and JKR theory to develop a modified JKR equation to solve the intrinsic problem of instrumented indentation system. Our experimental algorithm to exclude polymer time-dependency was designed to capture more static JKR contact conditions. Finally, we verified this algorithm through two materials, PDMS and Si-RTV, as shown in Table 3, and compared the results with the handbook reference shown in Fig. 16.

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