

RECENT PROGRESS OF NANO-MECHANICAL MAPPING

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Abstract Nano-mechanical mapping by atomic force microscopy has been developed as an useful application to measure mechanical properties of soft materials at nanometer scale. To date, the Hertzian theory was used for analyzing force-distance curves as the simplest model among several contact mechanics between elastic bodies. However, the preexisting methods based on this theory do not consider the adhesive interaction in principle, which cannot be neglected in the ambient condition. A new analytical method was introduced to estimate the elasticity and the adhesive energy simultaneously by means of the JKR theory, describing adhesive contact between elastic materials. Poly(dimethylsiloxane) (PDMS) and isobutylene-co-isoprene rubber (IIR) were analyzed to verify the applicable limit of the JKR analysis. For elastic samples such as PDMS, the force-deformation plots obtained experimentally were consistent with JKR theoretical curves. Meanwhile, for viscoelastic samples, especially for IIR, the experimental plots revealed large deviations from JKR curves depending on scanning velocity and maximum loading force. Some nano-rheological arguments were employed based on the difference between these specimens.

Keywords: Atomic force microscopy; Nano-mechanical mapping; Force-distance curve; JKR theory.

INTRODUCTION

Atomic force microscope (AFM)^[1] provides high-resolution topographic images at nanometer-scale for a variety of materials. It examines materials' surfaces by scanning a sharp probe on them with detecting the interaction force between surfaces and the probe. The cantilever deflection is the actual quantity to measure the force, the top of which has the sharp probe. It is possible to measure surface topography by the feedback control to keep the force constant if the surface is sufficiently hard. The high-sensitive force measurement at pico-Newton level is the key technology of AFM as well as its capability of high-resolution imaging.

We have developed a nano-palpation technique, in other words, nano-mechanical properties measurement^[2] based on the above-mentioned specific features of AFM for soft-materials. The nanometer-scale inhomogeneous materials such as polymer nano-alloys and polymer-based nano-composites have been our special concern. In addition to topographic information obtained by conventional AFM technique, our nano-palpation techniques can provide the mechanical information, which will open a novel materials science.

Nano-mechanical mapping is the extended technique of nano-palpation to map nano-mechanical properties such as elasticity and adhesion two-dimensionally as well as surface topography^[3, 4]. Though the detailed description will be made in the following sections, the measurement of force-distance curve (FC) is the key issue. The surface elasticity is calculated from the curve. Rubbery materials, one of the soft-materials, are soft and easy to be deformed. Therefore, the force exerted by a hard cantilever can deform their surfaces. The relationship between the force and the deformation can be thus regarded as microscopic stress-strain curve. The curve is then fitted with any contact mechanics in order to provide surface elastic modulus. Hertzian

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Invited lecture presented at the International Symposium on Polymer Physics, 2008, Xiamen, China

Received July 17, 2008; Accepted August 19, 2008

mechanics^[5] is the simplest theory among them. There have been such reports to date^[6, 7], while the combination of FC analysis with force-volume (FV) measurement becomes a very powerful tool to obtain elasticity mapping for inhomogeneous nano-structures. FV measurement is the method to realize two-dimensional arrays of FC measurements. This method enabled us to obtain elasticity mappings of various soft-materials at nanometer-scale, together with real topographic image free from sample deformation. Different from the case of hard materials, the imaging of soft-materials by any conventional AFM techniques gives false topography due to the sample deformation depending on local elasticity.

Nano-mechanical mapping has been employed to several material systems to date. For instance, natural rubber/ethylene propylene diene monomer rubber blend and elongated natural rubber were investigated to map the elasticity distribution^[8]. Carbon-black reinforced natural rubber was also examined to estimate its interfacial property^[9]. However, in these applications, we adopted Hertzian theory and argued only elastic modulus and therefore the analyses were under many restrictions. More seriously, the practical measurement must be performed under a certain condition to avoid other complex interactions such as adhesion and viscoelasticity and to obtain precise and correct results. The measurement in aqueous environment was a possible example, where we could suppress water capillary effect unavoidable in ambient condition.

In this paper, we describe our recent progress of nano-mechanical analysis to make it applicable to conditions where we cannot ignore the adhesive and viscoelastic effects. First, the contact mechanics that takes adhesive interaction into account, JKR theory^[10], is introduced. Then, we discuss the realistic applicable limit of this theory based on several experimental results. Furthermore, viscoelastic effect is treated experimentally and theoretically to some extent for the future progress of nano-mechanical mapping to be a “nano-rheological mapping” technique.

EXPERIMENTAL

Force-Distance Curve and Its Conversion to Force-Deformation Plot

The force-distance curve (FC) measurement is originally performed to calibrate the cantilever deflection with respect to the piezoelectric scanner displacement. The cantilever is moved vertically against the surface of hard calibration specimen. The cantilever deflection and piezoelectric scanner displacement are plotted. Multiplying the cantilever deflection, Δ , by cantilever's spring constant, k , results in the conversion to force value, F , based on Hooke's law. Thus, this plot is called as force-distance curve (FC). Figure 1 shows the schematic picture of the contact between AFM sharp probe and “soft” sample surface. In the figure, the cantilever and the probe are expressed as spring and sphere ball, respectively. The left figure depicts the condition that the apparent force exerted on the cantilever becomes zero due to the balance between elastic repulsive force caused by sample deformation and adhesive attractive force. We refer to this specific point as “zero point.” On the other hand, the

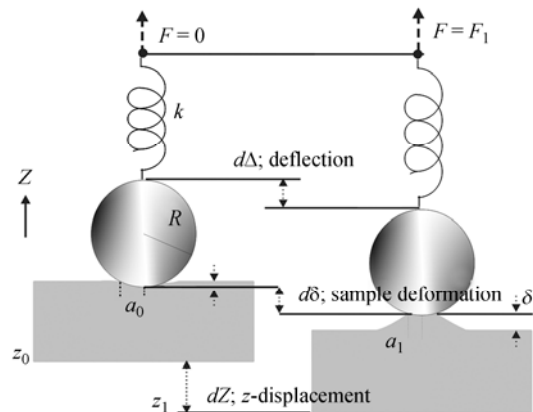


Fig. 1 Schematic drawings of the contact between AFM probe tip and adhesive surface where the tip feels balanced force (left) and the maximum adhesion force (right)

right figure describes the condition just before the rupture between the two bodies during withdrawing process. On this special occasion, the cantilever feels maximum adhesion force (negative sign). We refer to this point as “maximum adhesion point.”

Figure 2(a) shows the typical FC result taken for poly(dimethylsiloxane) (PDMS) rubber (open circles). If the sample is sufficiently hard compared with cantilever’s spring constant (rigid surface), FC becomes like dashed line just after a jump-in phenomenon. Then, the piezo displacement (dZ) and the cantilever deflection ($d\Delta$) are always equal to each other during the contact. However, on the soft surface like the case of PDMS rubber, dZ becomes the summation between $d\Delta$ and the sample deformation, $d\delta$, as schematically shown in Fig. 1, resulting in the non-linear curve like Fig. 2(a).

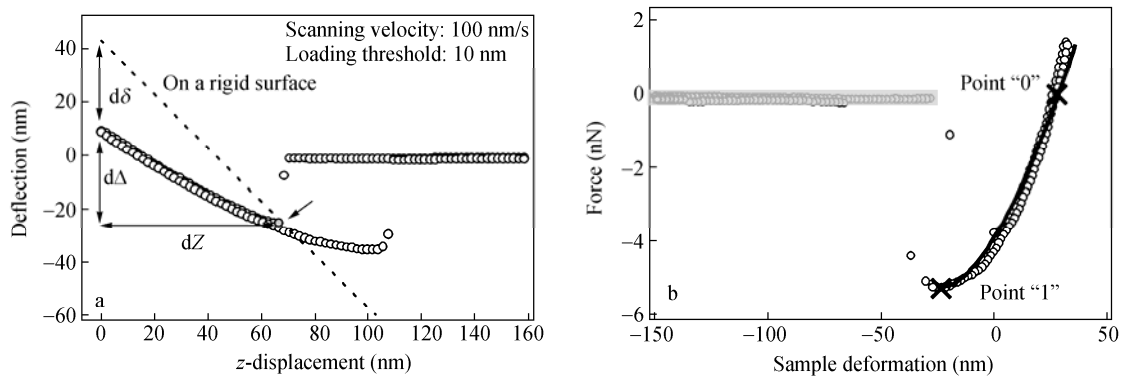


Fig. 2 (a) A representative force-distance curve for elastic sample, PDMS10, with additional line showing the force-distance curve for rigid surface. The arrow points to a contact point defined as the minimum force in the approaching curve. (b) The force-deformation plot of PDMS sample converted from the graph (a) with superimposed JKR theoretical curve

As given in the references [3] or [8] in more detail, we need to convert FC relationship to force-deformation (F - δ) plot to perform curve-fitting procedure. The conversion process is described below and the resultant F - δ plot for Fig. 2(a) is shown in Fig. 2(b): dZ , $d\Delta$, $d\delta$ have the relationship like

$$dZ = d\delta + d\Delta. \quad (1)$$

Thus, experimentally obtained dZ and $d\Delta$ give the estimation of $d\delta$. We define signs of these values: the sample compression corresponds to positive and the sample elongation to negative. In Fig. 1, for example, δ is slightly positive at zero point and is negative to the maximum at the maximum adhesion point. Here comes the question how to take the origin of deformation axis (contact point). In the references [3, 8], the measurements were free from jump-in phenomenon, and therefore the contact point could be regarded as the point where the cantilever deflection started to be positive (repulsive force). On the other hand, we have to treat the analysis based on JKR theory in this paper, and the adhesive interaction plays an important role. Thus, it is inevitable to treat FC with jump-in phenomenon. It is expected in this case that the force minimum point just after the jump-in in the approaching process can be the contact point (see arrow in Fig. 2a), although this argument is somewhat unclear because the situation is complicated depending on the sample nature and the cantilever’s spring constant. In addition, the direct observation of contact area is impossible in the current status of arts.

However, our calculation explained later uses merely the difference between the two sample deformation values. Thus, the relative value will serve the calculation. We, therefore this time, regard the origin of deformation axis as explained above (the point with an arrow in Fig. 2a). dZ now becomes the displacement from this contact point. Note that this calculation procedure produces imaginary sample deformation region to the negative direction even if the cantilever feels no more force (grayed area in Fig. 2b). This part is unreasonable and physically meaningless and therefore is to be omitted for the further calculation.

JKR Analysis

JKR analysis is introduced in this section. Hertzian analysis used the curve fitting in F - δ plot to calculate Young's modulus^[3, 8]. The mathematical formula for Hertzian contact is simple as follows,

$$F \propto C\delta^n, \quad (2)$$

where C includes material-dependent constant (Poisson's ratio) and the geometrical factors of the AFM probe. n also varies from 1 to 2 depending on the probe tip shape. Anyway, this closed-form expression was very much suitable for curve-fitting procedure. Oppositely, JKR formula is not so simple.

$$a^3 = \frac{R}{K} \left(F + 3\pi wR + \sqrt{6\pi wRF + (3\pi wR)^2} \right), \quad (3)$$

$$\delta = \frac{a^2}{3R} + \frac{2F}{3aK}, \quad (4)$$

where a , R , w are the contact radius, the radius of curvature for the probe tip and adhesive energy, respectively. K is called as elastic coefficient and has the relationship to Young's modulus, E , as follows,

$$E = \frac{3(1-\nu^2)}{4} K, \quad (5)$$

where ν is the Poisson's ratio. Any closed-form expression is not deduced from Eqs. (3) and (4) due to the existence of a , which is not an experimentally obtained value. There existed a report on the direct measure of contact radius between (rather large) particle and sample surface by scanning electron microscope^[11], it is not realistic for usual AFM measurement. Accordingly, the curve fitting like in the case of Hertzian contact is not nearly possible. In this paper, we adopted an alternative, the so-called "two-point method," introduced by Walker *et al.*^[12]. This is such a method that two special points from F - δ plot are used to calculate Young's modulus and adhesive energy algebraically.

These points are the two above-explained points: zero point ("0" in Fig. 2b) and maximum adhesion point ("1" in Fig. 2b). The subscript suffix put on physical quantities indicates these points from here in the rest of this paper, such as F_0 , δ_1 . F_1 is calculated from Eq. (3) as the condition that the formula inside square root becomes zero.

$$F_1 = -\frac{3}{2} \pi R w. \quad (6)$$

A simple transposition results in an expression of adhesive energy.

$$w = -\frac{2F_1}{3\pi R}. \quad (7)$$

Then, δ_0 and δ_1 can be calculated from Eqs. (3), (4) and (6) as follows using the equation $F_0 = 0$.

$$\begin{cases} \delta_0 = \frac{1}{3} \left(\frac{16F_1^2}{K^2 R} \right)^{1/3} \\ \delta_1 = -\frac{1}{3} \left(\frac{F_1^2}{K^2 R} \right)^{1/3} \end{cases} \quad (8)$$

These formulae finally come to the following expression of elastic coefficient,

$$K = \frac{1.27F_1}{\sqrt{R(\delta_0 - \delta_1)^3}}. \quad (9)$$

For example, $E = 2.2$ MPa and $w = 56$ mJ/m² for Fig. 2(b). In this case, k and R were not experimentally measured values and thus lacked quantitiveness, while these values have almost good coincidence with previous report^[13]. According to the report, Young's modulus of PDMS was *ca.* 0.4 MPa and surface free energy, γ , was *ca.* 22 mJ/m². Then, we could estimate the adhesive energy between PDMS and Si₃N₄^[14] to be about 90 mJ/m². The sequential substitution of these values for Eqs. (3) and (4) gave the JKR theoretical curve, which is superimposed in Fig. 2(b). As one can see, this theoretical curve reproduced the experimental curve quite well, indicating the effectiveness of the two-point method. However, the two-point method sometimes fails. This important argument will be made in the Results & Discussion.

Samples

Two kinds of cross-linked rubbery materials were selected as model specimens. They were isobutylene-co-isoprene rubber (IIR) and poly(dimethylsiloxane) (PDMS) rubber. PDMS rubber was prepared by using SYLGARD 184 (Dow Corning Toray Co., Ltd., Japan). The base and curing agents were mixed at appropriate ratios and cured at 80°C for 2 h. The curing agent concentration was set to 3% and 10%, both of which are referred to be PDMS3 and PDMS10, respectively. Figure 3 shows the dynamic viscoelastic measurements on these PDMS samples by conventional rheometer (HAAKE MARSII, Thermo Electron Corp., Germany). The measured specimen had the cylindrical geometry with diameter of 20 mm and height of 1 mm. The measurement was performed at room temperature. The shear strain was 0.01. The storage and loss moduli, G' , G'' at the strain rate of 10 Hz were plotted against the curing agent concentration. The frequency was swept from 0.1 Hz to 100 Hz, resulting in almost no change in modulus values. We could conclude from the figure that PDMS with the curing agent concentration from 5% to 20% showed very small loss tangent, while if the concentration was less than 5%, loss tangent increased. Thus, we will treat PDMS3 as viscoelastic sample and PDMS10 as elastic one. Figure 4 shows the dynamic viscoelastic measurements on IIR. The specimen was cylindrical in shape with diameter of 6 mm and height of 3 mm. The temperature dependence of G' and G'' from -40°C to 60°C was measured at shear strain of 0.001 and at the strain rate of 15 Hz. The clear peak of loss tangent was observed at around room temperature (*ca.* 12°C). Thus, IIR is expected to have strong frequency dependence on any room-temperature measurement.

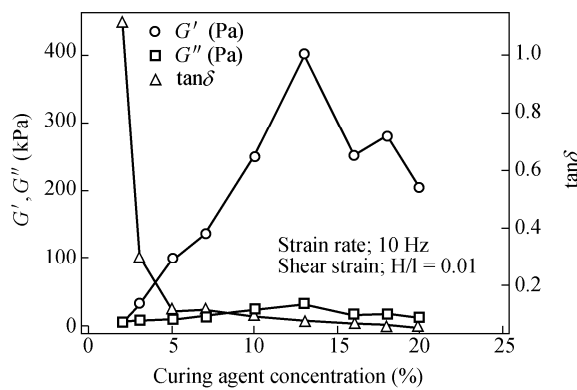


Fig. 3 The result of dynamic viscoelastic measurements for PDMS samples against the curing agent concentration at room temperature. The measurements were done at shear strain of 0.01 and strain rate of 10 Hz.

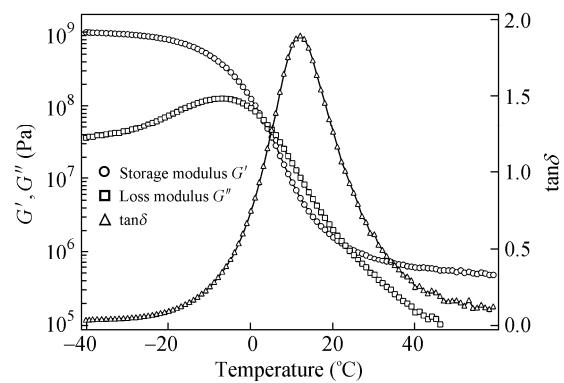


Fig. 4 The macroscopic values of storage and loss moduli and loss tangent for IIR sample obtained by dynamic viscoelastic measurement. Temperature dependence was measured in range from -40°C to 60°C at strain rate of 15 Hz. The peak of loss tangent appears in the vicinity of room temperature.

Instruments

NanoScope IV (Veeco Instruments, Inc., USA) was used. For the construction of two-dimensional arrays of FCs, force-volume mode was employed. Nano-mechanical analysis was performed by a homemade program running on Igor Pro (WaveMetrics, Inc., USA). The cantilever was OMCL-TR800PSA (Olympus, Co., Japan) with $k = 0.15$ N/m (nominal) or R150FM-10 (Nanosensors Inc., USA) with $k = 2.5$ N/m (nominal). It is possible to directly measure the spring constant by some experimental methods^[15, 16], though we used nominal values this time. However, an identical cantilever was used if relative comparison must be necessary.

OMCL-TR800PSA is designed for contact-mode operation in general and has conical probe tip. The probe was scanned over a sapphire surface to estimate the effective radius of curvature, R , to be about 20 nm, the value becomes no more valid when the sample deformation becomes larger. In order to apply JKR analysis, the probe tip must be approximated to be spherical shape. Thus, we tried the deformation value to be as small as possible. R150FM-10 is a commercially available spherical probe tip with $R = 150$ nm.

RESULTS AND DISCUSSION

The nano-mechanical mapping of IIR surface was shown in Fig. 5. As explained in the previous section, Young's modulus and adhesive energy mappings were realized with artifact-free real topographic image. It seems that analysis result is good enough, while there existed several problems in reality. Figure 6 shows two typical F - δ plots selected from Fig. 5. The calculated values were valid, and there were good agreements to each other at a glance. However, the experimental and JKR theoretical plots were almost identical in Fig. 6(a), though those in Fig. 6(b) had a certain discrepancy to each other. Thus, we could not believe that all of analyzed data were correct.

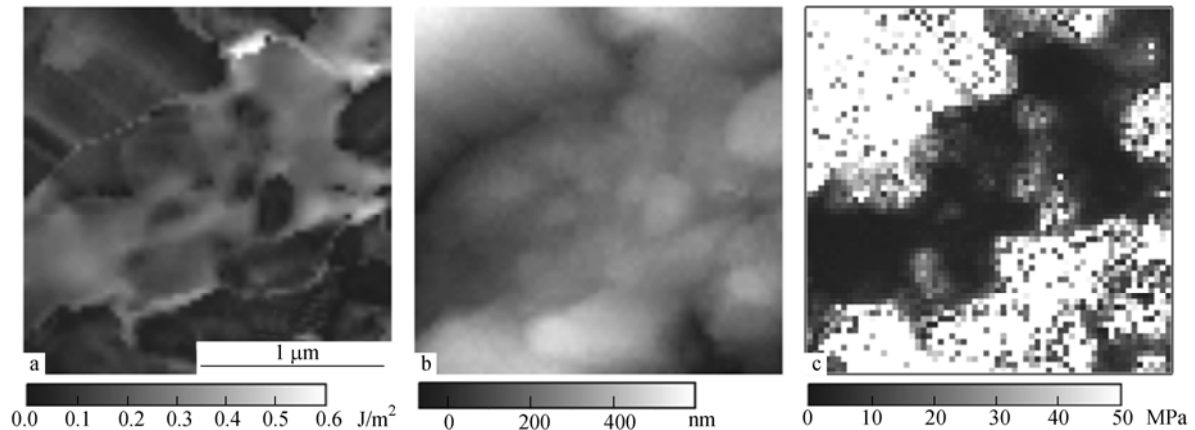


Fig. 5 The nano-mechanical mappings of IIR analyzed by JKR method

The images of (a) adhesive energy, (b) actual height and (c) Young's modulus at the same position; The measurement was performed by conical probe ($R = 20$ nm).

Then, it is necessary to discuss why such a difference emerged even on a single specimen surface. It is an appropriate argument judging from the previous reports on natural rubber^[17, 18] that cross-linked rubbery surface sometimes has nanometer-scale inhomogeneity. However, we should not forget about the fact that there was a clear discrepancy between experimental and theoretical plots. Such a discrepancy was never observed in the case of natural rubber.

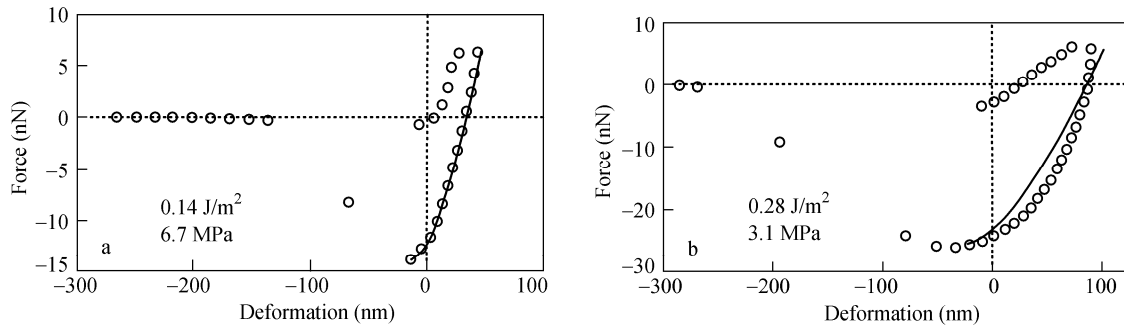


Fig. 6 Two of different force-deformation plots selected from the same force volume results in Fig. 5. The curve in (a) shows good agreement between JKR theoretical curve and the experimental plot, while that in (b) exhibits some deviation between them.

In order to elucidate the origin of deviation, further investigation was made as follows. Figures 7 and 8 show a series of F - δ plots in withdrawing (unloading) processes for IIR and PDMS10, respectively. In both cases, F - δ plots were taken at a single point on each surface with different scanning velocities. Other experimental conditions were kept identical. It was clear from Fig. 7 that F - δ plots for IIR varied remarkably depending on the velocities. The JKR theoretical curves were also superimposed on the slowest (200 nm/s), middle (6.0 μ m/s) and the fastest (60 μ m/s) velocities. The slowest and the fastest curves were in sufficiently good agreement to respective experimental curves. On the other hand, the result on 6 μ m/s velocity failed to reproduce the experimental curve.

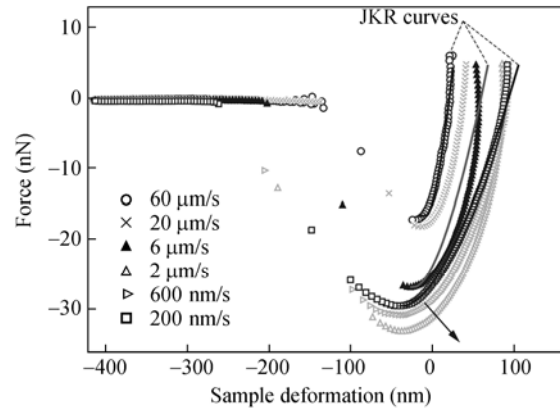


Fig. 7 Dramatic change of F - δ plots obtained from IIR at different scanning velocities by conical probe ($R = 20$ nm). JKR fitting curves for 200 nm/s and 60 μ m/s experimental plots are overlapped.

More detailed look told us that the experimental curves for the slower velocities indicated soft behavior and those for the faster velocities indicated rigid behavior. This observation was confirmed by the obtained Young's modulus values. The velocity of 200 nm/s gave 3.2 MPa, while that of 60 μ m/s gave 10.2 MPa. We are speculating that this curious behavior is strongly correlated with glass-rubber transition seen in bulk material at room temperature as shown in Fig. 4^[2]. The glass-rubber transition occurs at nanometer-scale. The region of slower velocities from 200 nm/s to 600 nm/s exhibited rubbery feature. Considering the slight increase in adhesive energy on increasing velocity, some type of velocity-dependent energy dissipation would be involved in the observed phenomena, which will be a future discussion. Similarly, the velocity region near 6.0 μ m/s exhibited transition state, and the faster velocities (20 μ m/s and 60 μ m/s) exhibited glassy feature.

It is possible to test the validity of JKR analysis using Tabor's equation^[19, 20]. The dimensionless parameter

μ is expressed as follows;

$$\mu = \left(\frac{Rw^2}{E^2 D_0^3} \right)^{1/3}, \quad (10)$$

where D_0 is called as equilibrium separation between surfaces and is in general in the range of 0.3–0.5 nm. It is said that JKR analysis is appropriate if $\mu > 5$. Assume that $D_0 = 0.3$ nm, we estimated this Tabor parameters for velocities of 200 nm/s (rubber) and 60 $\mu\text{m/s}$ (glass). Both were 190 and 62 and fulfilled the criterion. We could conclude that these regions were within applicable limit of JKR analysis. However, as was the same with Fig. 6(b), F - δ plots for 2.0 and 6.0 $\mu\text{m/s}$ showed heavily curved features and therefore were never fitted with JKR theory. This would be due to larger energy loss or surface-specific energy dissipation.

In contrast to IIR, PDMS10 showed less velocity-dependent results in Fig. 8. Three curves coincided with each other, and JKR analysis fairly reproduced the experimental results. PDMS10 could be regarded as an almost perfect elastic body because of its sufficiently small loss tangent at room temperature (see Fig. 3). Thus, we can expect that practically elastic materials are well described within the framework of JKR theory independent on scanning velocities. The nano-mechanical mapping of PDMS10 is shown in Fig. 9. The measured E and w were almost homogeneous. JKR theoretical curves were also in good agreement with the

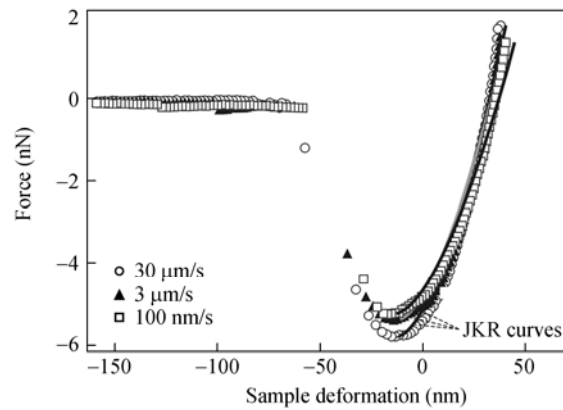


Fig. 8 F - δ plots of PDMS10 at different scanning velocities by conical probe ($R = 20$ nm) with JKR curve fitted to 100 nm/s experimental plot

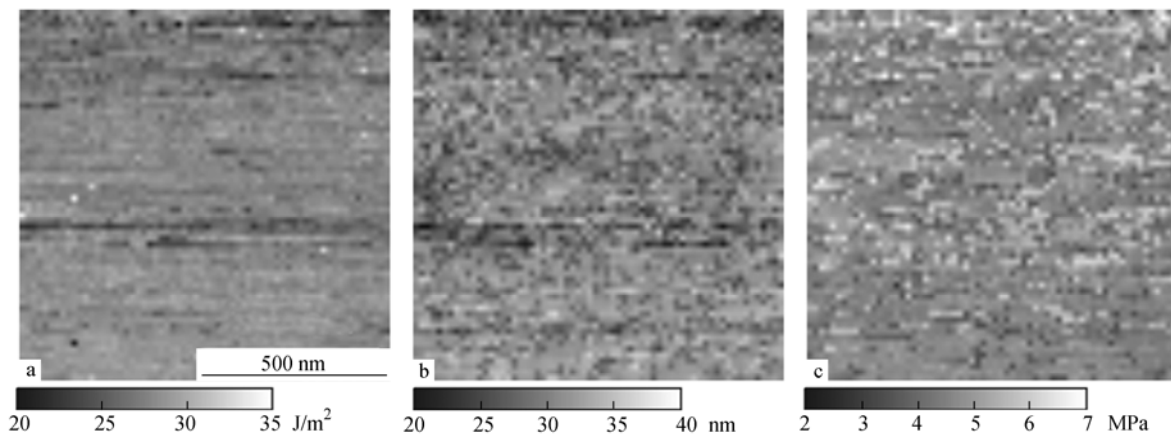


Fig. 9 Nano-mechanical mappings obtained from PDMS10 by conical probe ($R = 20$ nm) Contrary to Fig. 5, the mappings of (a) adhesive energy, (b) topography and (c) Young's modulus at the same position display homogeneous feature.

experimental curves. Thus, the nano-mechanical evaluation could be regarded to be more accurate in this case. Here comes the conclusion that JKR analysis is only applicable to sufficiently elastic materials, and it is beyond an applicable limit for viscoelastic materials such as IIR.

For more detailed discussion about viscoelastic effects, we plotted the relationship between E or w determined by the two-point method and maximum sample deformation as shown in Fig. 10. In practical experiments, we varied the scanning velocity and the maximum loading force. The larger the maximum loading force became, the larger the maximum sample deformation were attained. Because the two-point method failed to represent experimental curves at some conditions as we have discussed above, the obtained E or w must be treated as apparent values. However, interestingly, Young's modulus changed monotonously on maximum sample deformation for IIR. PDMS3 or PDMS10 gave almost constant modulus in contrast.

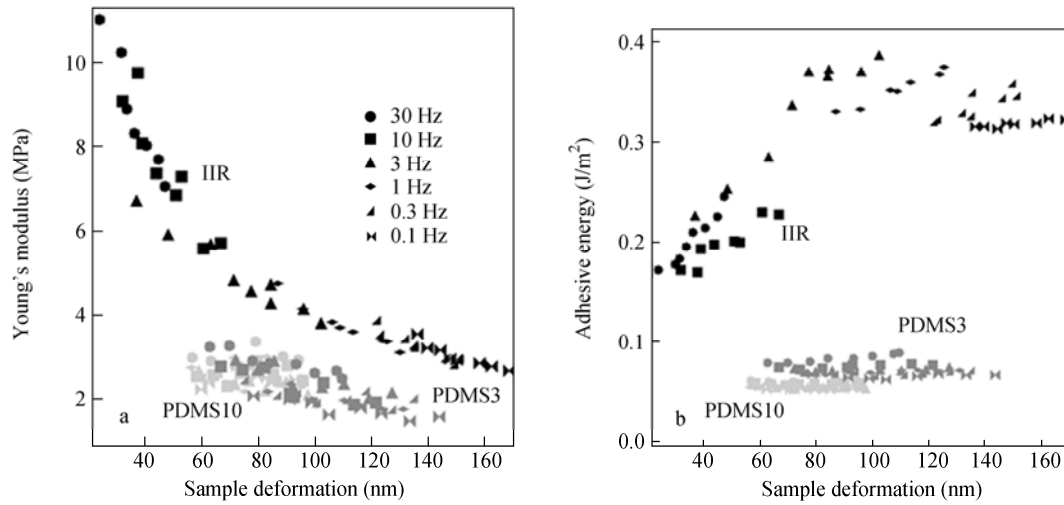


Fig. 10 (a) Young's modulus and (b) adhesive energy of IIR (black), PDMS3 (dark gray) and PDMS10 (light gray) at different scan rates plotted as a function of maximum sample deformation. All results were obtained by conical probe using 20 nm for tip radius, R , for calculation.

Similar observation could be made for adhesive energy. The adhesive energy must be intrinsically constant not depending on any experimental parameters like in the case of PDMS10. However, PDMS3 showed a little deviation and IIR showed a large deviation. This is of course due to the failure of JKR analysis, but we are thinking that these deviations contain fruitful information about nanometer-scale rheological phenomena.

It has been proved that adhesive energy can be a function of crack propagation speed according to Maugis's theory^[21]. Here in the case of AFM experiment, crack propagation occurs at the interface between the probe surface and the sample surface. By this theory, strain-energy release rate G is expressed by a dimensionless function of crack propagation speed v and WLF shift factor a_T as follows,

$$G - w = w\phi(a_T v). \quad (11)$$

Here G can be treated as apparent adhesive energy, and the condition $G = w$ is accomplished in equilibrium state. The function $\phi(a_T v)$ represents viscoelastic loss at the crack front and is indeed a power function of v . The detailed analysis will be given elsewhere, while this equation supports a little bit increase in adhesive energy at elevated scanning velocity for PDMS3. However, the theory does not sufficiently explain the phenomena observed in IIR. We should consider probe shape effect for further discussion. Actually, experimental data in Figs. 5–10 were taken by conical probe. Then, a small change in radius of curvature R due to a change in contact area becomes trivial compared to serious shape change. We treated the tip of conical probe as spherical as the first approximation, while we must not forget the original conical shape when the sample deformation becomes large enough.

In order to check the loading-force dependence as seen in Fig. 10 more strictly, we used spherical probe with $R = 150$ nm for PDMS3 (somewhat viscoelastic) and PDMS10 (elastic) as shown in Fig. 11. The experimental parameter was the maximum loading rate and thus the maximum cantilever deflection. Because of the spherical probe, R in JKR theory was perfectly fixed. PDMS10 in Fig. 11(b) showed a good trace with changes only in the maximum loading force. JKR analysis worked very well. In addition, loading and unloading processes possessed the same trace. On the other hand, PDMS3 in Fig. 11(a) showed a hysteresis between the loading and the unloading processes. The hysteresis became larger when the loading force was increased. The degree of discrepancy between the experimental and the theoretical curves was also enlarged. This observation brought us to the conclusion that viscoelastic materials were strongly affected by the maximum loading force due to mechanical loss. The analyzed values were summarized in Table 1. Young's modulus decreased in both cases. The amount is not comparable to the case of PDMS3, though viscoelastic nature began to emerge even in the case of PDMS10 when the loading force became larger. The loading force was less effective in the estimation of adhesive energy.

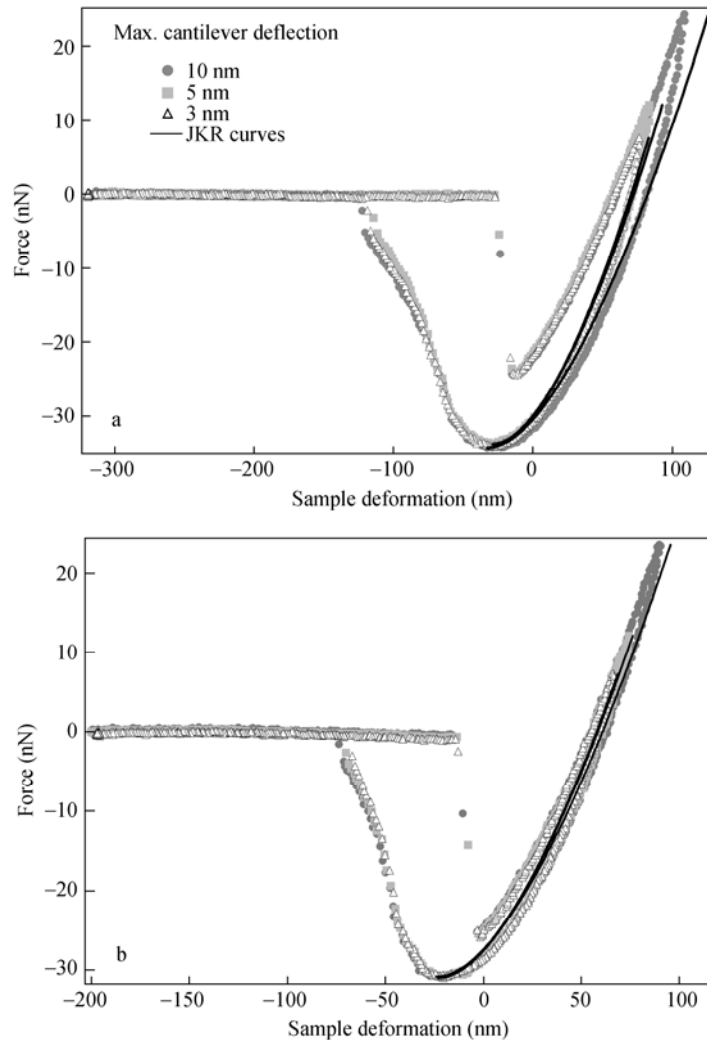


Fig. 11 The maximum loading force dependence of F - δ plots obtained from (a) PDMS3 and (b) PDMS10 by spherical probe ($R = 150$ nm)

Table 1. The values of Young's modulus and adhesive energy calculated from two sets of force-deformation plots in Fig. 11 (a) PDMS3 and (b) PDMS10

	Max. deflection (nm)	E (MPa)	w (J/m ²)
PDMS3	3.0	2.1	0.048
	5.0	2.0	0.048
	10.0	1.7	0.049
PDMS10	3.0	2.6	0.044
	5.0	2.5	0.044
	10.0	2.4	0.044

CONCLUSIONS

We discussed the recent progress of nano-mechanical properties evaluation based on JKR analysis. The sufficiently elastic materials such as PDMS10 could be treated within this framework, while the viscoelastic nature caused large deviation from JKR theory like the case of PDMS3 or IIR. In order to investigate viscoelastic effect, experiments varying scanning velocity and the maximum loading force were performed. We are continuing to develop a theory that can treat viscoelastic materials, while the argument on the applicable limit of JKR theory reported in this paper would be very helpful for the better understanding of future nano-rheological analyses.

ACKNOWLEDGMENT Authors are grateful to Dr. D. Kaneko and Dr. H. Morita at the University of Tokyo for their help in sample preparation and dynamic viscoelastic measurements on PDMS specimens. Authors are also grateful to Dr. S. Hamatani and Dr. K. Akutagawa at Bridgestone, Co. for their help in dynamic viscoelastic measurements on IIR specimens. The authors thanks for the financial support from National Institute of Advanced Industrial Science and Technology (AIST), Japan Chemical Innovation Institute (JCII) and New Energy Development Organization (NEDO) as one of the projects in the Nanotechnology Program by the Ministry of Economy, Trade, and Industry (METI) of Japan.

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