

Feature Article

STRUCTURE AND DYNAMICS OF POLYMERIC MATERIALS IN NANO-SCALE

Toshio Nishi*, So Fujinami, Dong Wang, Hao Liu and Ken Nakajima
WPI Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Abstract The nano-palpatation technique, *i.e.*, nanometer-scale elastic and viscoelastic measurements based on atomic force microscope, is introduced. It is demonstrated to be very useful in analyzing nanometer-scale materials properties for the surfaces and interfaces of various types of soft materials. It enables us to obtain not only structural information but also mechanical information about a material at the same place and at the same time.

Keywords: Nano-palpatation; Atomic force microscope; Soft material; Young's modulus; Viscoelasticity.

INTRODUCTION

Recently, there have been many attempts to develop nano-structured polymeric materials to satisfy the ever-increasing demand to accommodate a green and sustainable society. This demand requires such materials to be multi-functional and of high performance. Therefore, research and development into structure optimization and related processing development for polymer alloys and polymer-based composites have become more important subjects. This situation accelerates the development of evaluation techniques that have nanometer-scale resolution. To date, transmission electron microscopy (TEM) has been widely used for this purpose. However, TEM technique cannot probe the mechanical properties of such materials in general. The realization of much higher performance materials requires an evaluation technique that enables us to investigate topological and mechanical properties at the same point and the same time. Atomic force microscopy (AFM)^[1] is clearly an appropriate candidate because it has almost comparable resolution with TEM. Furthermore, mechanical properties can be readily obtained by AFM due to the fact that the sharp probe tip attached to the soft cantilever directly touches on the materials in question.

However, there are several drawbacks in AFM usage for polymeric materials. For example, the sample deformation caused by the force between the probe tip and the sample can lead to mistaken interpretation of the obtained topography. The tapping-mode phase contrast image is difficult to interpret or provides at most qualitative information. We have been engaged for many years in using AFM with a sufficient understanding of its advantage and disadvantage in order to develop methodology suitable for polymeric soft materials, namely, nanorheology^[2] and nanotribology^[3, 4]. The peculiar feature of these methods is the positive usage of sample deformation. We are able to extract mechanical information on polymeric materials from the sample deformation. Due to this fact, we may refer to this method as a nano-palpatation technique^[5, 6], where a doctor's finger is replaced by the sharp AFM probe tip. In order to realize this idea, analyses of force-distance curves have proven to be powerful, and correspond to macroscopic stress-strain curves. In the analysis, sample deformation and force exerted are quantitatively estimated to acquire a true topographic image free from the

* Corresponding author: Toshio Nishi, E-mail: nishi.toshio@wpi-aimr.tohoku.ac.jp

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effect of sample deformation together with a Young's modulus image^[7–14], an adhesive energy image^[15–17] and an energy dissipation image at the same time.

In this presentation, we review the applications of this method to several polymeric materials, including polystyrene (PS)/poly(methyl methacrylate) (PMMA) immiscible blend, reactive-compatible blend, polyolefin elastomer (POE)/polyamide (PA6)^[18]. We also present the further extension of this method to investigate viscoelastic properties of polymeric materials.

METHOD

AFM as Nano-palpation

The sample deformation caused by direct touch of the AFM sharp probe is inevitable in AFM usage. If this effect is negligible, an obtained image expresses a true surface topography. However, soft-materials are easily deformed even by a very weak force. Plastic materials having a GPa-order Young's modulus might not be deformed significantly by pN to nN-level force, whereas rubbery materials with a MPa-order modulus and gels with a kPa-order modulus undergo substantial deformation. This effect might become a disadvantage for the request to have true topography, while we can measure the surface Young's modulus because of this effect. Like body palpation by medical doctors or masseurs, we can now perform nano-palpation with the AFM sharp probe enabling measurement of surface elasticity.

Contact Mechanics

The simplest theory for the analysis of surface elasticity based on AFM force-distance curve measurements is Hertzian contact mechanics^[19]. However, we must consider the case is rather special where adhesive forces are negligible. If adhesive effects are no longer negligible, one must switch to the adhesive contact model developed by Johnson, Kendall and Roberts (JKR model)^[20]. Figure 1(a) shows a schematic picture of adhesive contact during the unloading process. Figure 1(b) is the schematic force-distance curve during loading and unloading processes. First, it is observed that an abrupt change in cantilever deflection occurs from the point $(z_c, 0)$ to the contact point (z_c, Δ_0) . After that, the force increases, crossing the horizontal axis $(z_0, 0)$ in Fig. 1(b), where the apparent force exerted on the cantilever becomes zero due to the balance between the elastic repulsive force caused by sample deformation and the adhesive attractive force (balance point). During the unloading process, a much larger adhesive force is observed beyond the original contact point. The sample surface is raised up during this time. Finally, the maximum adhesive force is realized (maximum adhesion point) at (z_1, Δ_1) in Fig. 1(b), succeeded by a sudden decrease of contact radius and jump-out of the cantilever.

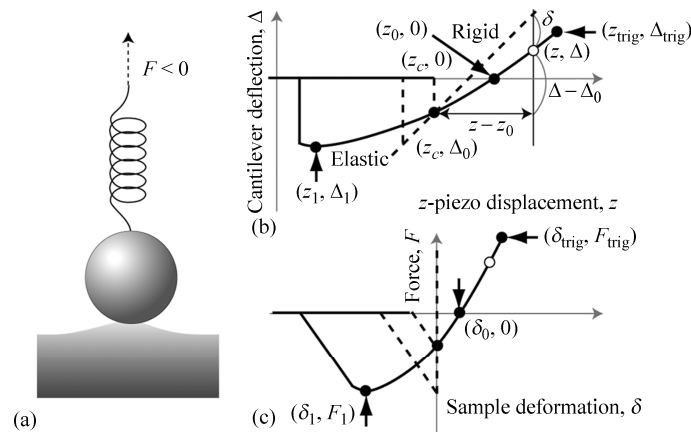


Fig. 1 Analysis procedure for force-distance curves with an adhesive force between sample and AFM probe
a) Schematic of adhesive contact when the applied force is negative (attractive); b) The force-distance curve for adhesive contact; c) The corresponding force-deformation plot

The AFM cantilever and probe are treated as a spring with the spring constant of k and a sphere with radius of curvature, R , respectively. The force, F , is expressed by Hooke's law,

$$F = k\Delta. \quad (1)$$

The sample deformation is calculated by the formula,

$$\delta = (z - z_c) - (\Delta - \Delta_0) \quad (\Delta_0 < 0). \quad (2)$$

Using this equation, the z - Δ plot in Fig. 1(b) is converted to δ - F plot shown in Fig. 1(c). JKR contact is described as follows^[20],

$$F = \frac{K}{R}a^3 - 3w\pi R - \sqrt{6w\pi R F + (3w\pi R)^2} \quad (3)$$

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

where a is the contact radius, w is called as the adhesive energy. K is the so-called elastic coefficient and is expressed using the reduced Young's modulus E^* as follows,

$$K = \frac{4}{3}E^* = \frac{4}{3} \left[\frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_p^2}{E_p} \right]^{-1}, \quad (5)$$

where E_i and ν_i are Young's modulus and Poisson's ratio, respectively. The subscript i stands for sample (s) and probe (p). Since Eq. (4) is a cubic equation of a , a closed-form expression can not be deduced from Eqs. (3) and (4). There exists a report on the direct measurement of the contact radius, a , between a large particle and the sample surface by scanning electron microscopy (SEM)^[21], which is not realistic for typical AFM measurements. Thus, as an alternative, the so-called "two-point method" has been used, which was introduced by Walker *et al.*^[22]. This method involves the use of two special points from δ - F plot is used to calculate Young's modulus and adhesive energy algebraically.

These points are the above-explained two points: the balance point ($\delta_0, 0$) and the maximum adhesion point (δ_1, F_1) in Fig. 1(c). Using the values for these points, Eqs. (3) and (4) finally lead to the following expression for the elastic coefficient and adhesive energy^[6],

$$K = \frac{1.27F_1}{\sqrt{R(\delta_0 - \delta_1)^3}}, \quad (6)$$

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

Nano-mechanical Mapping

AFM is widely used in the world as an imaging tool for soft-materials. Contact and tapping-mode operations are known as the major imaging modes. Specimens are scanned over their surfaces with mechanical contact in both modes. Thus, it has been recognized among researchers that topographic images from both modes may be affected by the deformation of the sample itself due to the contact or tapping forces. Users may also have been able to qualitatively understand the influence of contact or tapping forces on experimental topographic images in the past. However, AFM imaging with a constant force condition never results in quantitative estimation of such influences.

Now, here is demonstrated a quantitative method to obtain accurate topographic images of deformable samples together with Young's modulus and adhesive energy distribution images^[7, 12]. The value of the cantilever spring constant, k , is an important factor in detecting mechanical properties from a sample surface. If k is very small, the cantilever approaching the surface cannot deform the sample. If k is very large, however, the

cantilever can deform the sample, without any deflection. Therefore, necessary information about the sample is not detected. Thus, we need to choose a cantilever with an appropriate value for k .

To map the local mechanical properties of soft materials, force-volume (FV) measurement is the most appropriate method. In this mode, force-distance curve data are recorded until a specified cantilever deflection value (trigger set-point), Δ_{trig} , is attained for 128×128 points over a two-dimensional surface. At the same time, z -displacement values, z_{trig} , corresponding to the trigger set-point deflection are recorded to build an apparent topographic image. The topographic image taken in this mode is basically the same as that obtained by the conventional contact mode if the contact force set-point and the trigger set-point are identical. If all the points over the surface are rigid enough, the set of recorded displacements, z_{trig} , represents the topographic image (true height) of the sample. However, if the surface deforms as discussed, it is no longer valid to regard the obtained data as the true topographic information. However, since we have a force-distance curve for each point, we can estimate the maximum sample deformation value for each point, referring to Eq. (2),

$$\delta_{\text{trig}} = (z_{\text{trig}} - z_c) - (\Delta_{\text{trig}} - \Delta_0) \quad (\Delta_0 < 0), \quad (8)$$

where $\Delta_0 = 0$ for non-adhesive contact. Consequently, two-dimensional arrays of sample deformation values can be regarded as the sample deformation image. The force-distance curve analyses for 16384 data yield the Young's modulus distribution and adhesive energy distribution images at the same time and the same location. We now have apparent height (z_{trig}) and sample deformation (δ_{trig}) images taken at the same time and Δ_{trig} is the preset value and therefore constant for all of the force-distance curves. Then, the appropriate determination is performed for the contact point (the array of (z_c, Δ_0)), this realizes the reconstruction of the "true" surface topography, free from sample deformation^[7, 12].

RESULTS AND DISCUSSION

PS/PMMA Immiscible Blend

PS ($M_n = 190000$, $M_w = 197600$) and PMMA ($M_n = 46400$, $M_w = 93000$) was blended at 5:5 ratio and spin-coated on a cover glass as the test specimen. The glass transition temperature (T_g) of each polymer was measured by differential scanning calorimetry (DSC). T_g of 107°C was obtained for PS, while that of 108°C was for PMMA. As imagined from the close coincidence of T_g , they are mechanically similar to each other at room temperature. This is experimentally verified by conventional tapping-mode AFM imaging as shown in Fig. 2. The free amplitude of the cantilever was 40 nm and the amplitude setpoint was about 0.73. The spring constant of the cantilever, k was measured to be 2.4 N/m. One can hardly distinguish the difference between the phase values on the island and matrix (at most 1° on average). The drive frequency of the AFM cantilever used in this experiment was 63 kHz. The mechanical responses of both polymers to such a high frequency must be negligible^[23]. On the other hand, the result of the nano-mechanical mapping is shown in Fig. 3. It was possible to clearly distinguish the difference in the deformation and Young's modulus images. The measured k was 1.7 N/m and the force-distance curves were obtained at the scan rate of 6.5 Hz. Δ_{trig} was set to be 20 nm. The average Young's modulus on the island was 3.5 GPa and that on the matrix was 2.5 GPa. We can conclude that our nano-mechanical mapping can be successfully used to map the very subtle difference in the modulus value. Since the matrix is softer, the deformation is larger, resulting in the higher contrast in the true height image. Figure 4 show the relationship between apparent height, true height and sample deformation. From this discussion, it was also inferred that tapping-mode height image shown in Fig. 2(a) was not the true height, though the tapping force was much smaller than the trigger force used for Fig. 3. Although data are not shown here, it was performed the similar measurement using the softer cantilever (0.06 N/m) to map the difference in adhesive interaction. The island showed the larger adhesive force due to hydrophilic interaction with the AFM probe made of Si. The surface of the probe is somewhat oxidized and therefore rather hydrophilic. According to these results, we could judge that the island is composed of PMMA and the matrix is composed of PS.

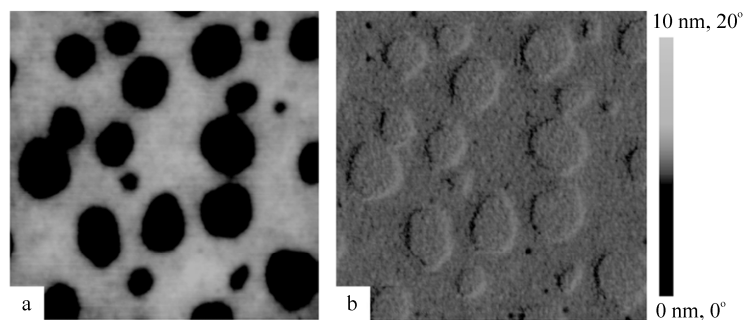


Fig. 2 Tapping-mode AFM images of PS/PMMA immiscible blend (scan size: $1.0\ \mu\text{m}$): (a) topographic and (b) phase-contrast images

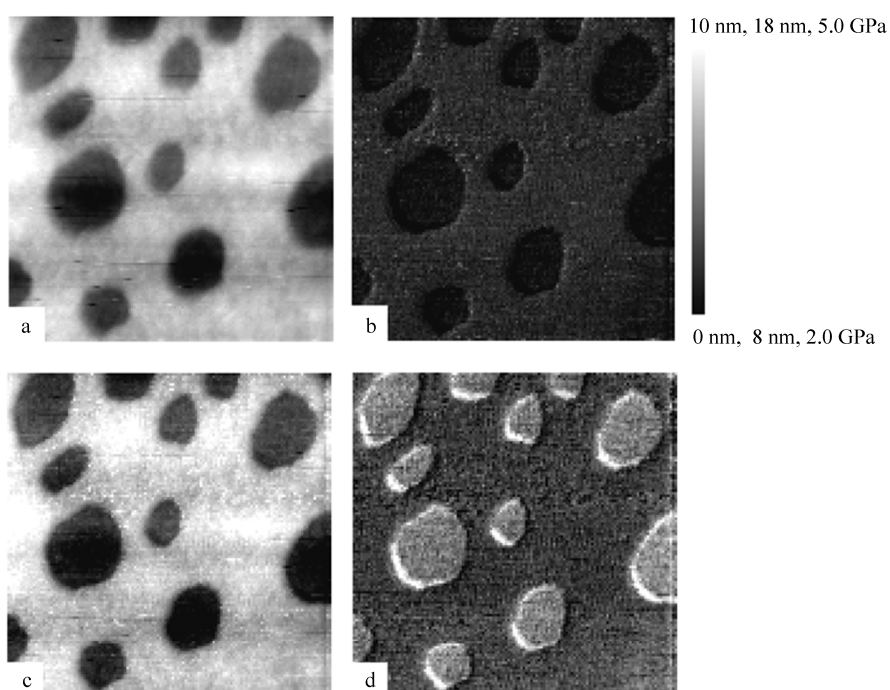


Fig. 3 Nano-mechanical mapping of PS/PMMA immiscible blend (scan size: $1.0\ \mu\text{m}$): (a) apparent topographic (scale bar: 0–10 nm), (b) deformation (scale bar: 8–18 nm), (c) true topographic (scale bar: 0–10 nm) and (d) Young's modulus (scale bar: 2.0–5.0 GPa) images

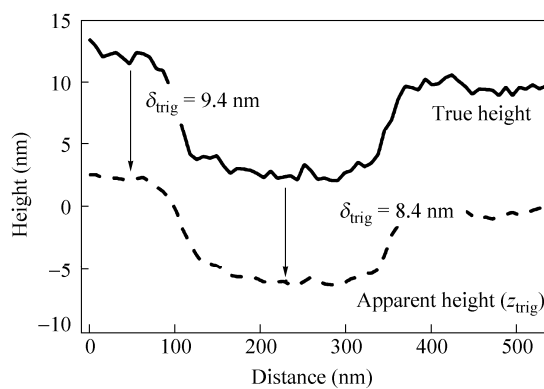


Fig. 4 The cross-sectional profiles of apparent height (dashed line) and true height (solid line)

Reactive-compatible POE/PA6 Blend^[18]

Compatibilization of immiscible polymer blends is a convenient way for obtaining high-performance polymeric materials. For this purpose the following two methods are usually used: one is the addition of premade block or graft copolymer during mixing of the immiscible blends, and the other is reactive compatibilization in which the block or graft copolymer is formed *in situ* at the interfacial regions. The pre-added or *in situ* formed copolymer is believed to play the role of an emulsifier, which promotes compatibilization and increases interfacial adhesion between the immiscible polymers. Therefore, investigation of the polymer-polymer interface in such blends has been a long-standing academic and technological challenge. TEM is an important technique for characterization of the interfacial morphology. The interfacial thickness and emulsified region can be measured by examining the cross section of the interface^[24]. However, staining is usually necessary for contrast, limiting the types of model polymers available for testing. For some polymer pairs such as polyolefin/nylon and polyolefin elastomer/nylon, the double-staining technique is necessary to deeply stain the interface to get better contrast^[25], which sometimes is difficult or inconvenient to perform. Most importantly, TEM never catch mechanical information on the constituting polymers and interfacial regions. We used the above-mentioned nano-palpation AFM to investigate this subject.

Uncompatibilized POE/PA6 (80/20) and reactive-compatible POE grafted maleic anhydride/PA6 (POE-g-MA/PA6) (80/20) blends were prepared with a micro twin-screw extruder. The resulting blends were first cut using an ultramicrotome at -120°C to obtain a flat surface. The formation of block or graft copolymer by coupling reaction between anhydride/amine leads to a fine morphology and increases the interfacial adhesion of such immiscible blends. The tapping-mode topographic images of uncompatibilized and compatibilized specimens are shown in Fig. 5. As expected, the dispersion and particle size of the dispersed phase PA6 becomes homogeneous and displays a very fine dispersion due to the reactive compatibilization. MA groups in compatibilizer react with amine groups in PA6 to form copolymers, which induces a drastic decrease in interfacial tension and suppression of coalescence between the originally immiscible polymer phases.

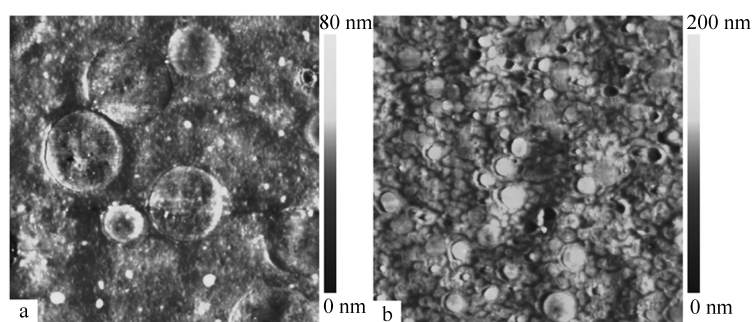


Fig. 5 Tapping-mode topographic images of (a) uncompatibilized POE/PA6 (scan size: $12.0\ \mu\text{m}$) and (b) reactive-compatible POE-g-MA/PA6 (scan size: $10.0\ \mu\text{m}$)

Figure 6 shows the Young's modulus map of uncompatibilized POE/PA6 and reactive compatible POE-g-MA/PA6 blends. Note that the scan area is decreased to $500\ \text{nm}$ to focus on the interface between a particle and a matrix. The left half area in Fig. 6(a) and the right half area in Fig. 6(b) show higher Young's modulus and are assigned to the disperse phase PA6 component, while the matrix areas show lower modulus are assigned to the POE or grafting POE component. The Young's modulus calculated *via* the δF plot is (2.9 ± 1.1) GPa for PA6 component and (25.5 ± 10.3) MPa for POE or grafting POE component. The Young's modulus of both PA6 and POE components agrees well with bulk modulus (PA6: (2.5 ± 0.9) GPa; POE and POE-g-MA: (23.5 ± 11.1) MPa). Thus, we may claim that the nanomechanical mapping technique is successful for identifying the composition in those blends.

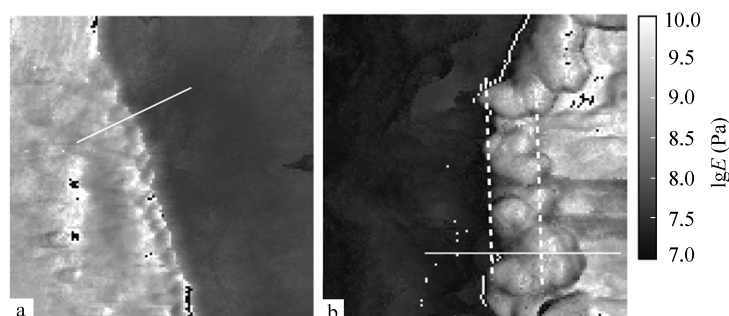


Fig. 6 Nano-mechanical Young's modulus images of (a) uncompatibilized POE/PA6 (scan size: 500 nm) and (b) reactive-compatible POE-g-MA/PA6 (scan size: 500 nm)

As shown, the interface between the POE and PA6 in uncompatibilized blend is smooth and flat, whereas for the compatibilized blends the interface becomes quite rough after the same processing. Some parts of the POE domain appear to have pinched off at the interface and moved into the PA6. We approximately localize the roughening zone using two dashed lines in Fig. 6(b). The magnitude of the width of the roughening zone is about 70 nm. A line section across the interface indicated by the solid line in Fig. 6 shows the transition between Young's modulus of the two polymer phases in uncompatibilized blend is sharp while it becomes much wider in the compatibilized blend (Fig. 7). We call the transition distance that Young's modulus increases from that of POE to that of PA6 as the interfacial width. The interfacial width for uncompatibilized blend is *ca.* 12 nm and, after reactive compatibilization, it increases to *ca.* 31 nm. It should be noticed that the occurrence of the interfacial width in the uncompatibilized blend is probably caused by small Flory's interaction parameter (χ) or thermal fluctuations^[26, 27]. In conclusion, nano-palpatation AFM enables us not only to measure the Young's modulus map of the blend components but also to quantitatively discuss the interfacial morphology, the interfacial width and its mechanical property.

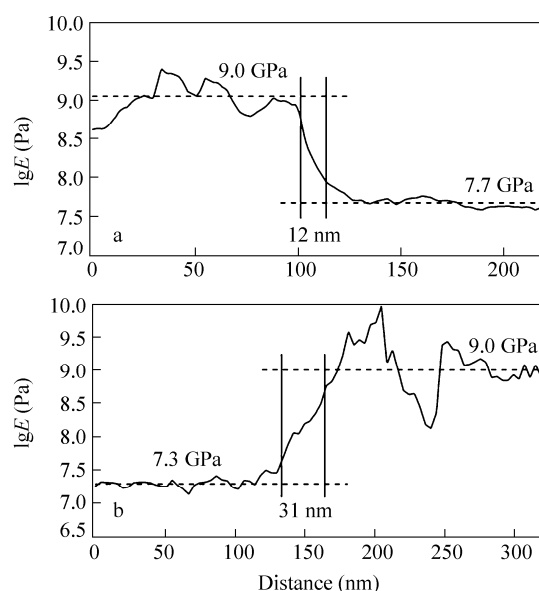


Fig. 7 Line profiles (a) and (b) along the solid lines in Figs. 6(a) and 6(b), respectively

Visualization of Viscoelasticity

As reviewed above, we established a nano-mechanical properties mapping method, in which force-distance curves are measured at various points of the sample surface and elastic properties given by the curve and elastic

mechanics model are mapped as a two dimensional image on nanometer scale. While this technique showed great usefulness to investigate nanomechanical properties of various elastic materials, Hertz and JKR theories of elastic mechanics, mostly adopted in the analyses, do not take viscoelasticity into consideration. However, we found force-distance curves on viscoelastic materials deviate largely from those theories^[15, 16]. Here we describe the method to visualize viscoelastic properties. We prepared natural rubber/isoprene-*co*-isobutene rubber (IIR) 7:3 blend as a model specimen. Glass transition temperature of NR and IIR is -70°C and -10°C , respectively. Therefore NR acts as an elastic body and IIR is viscoelastic at room temperature.

Figure 8(a) shows the topographic image derived in the measurement. Analyzing every curve with Eqs. (6) and (7), the distribution of Young's modulus and adhesive energy can be derived. Figure 8(b) is the Young's modulus image. Although data not shown for the adhesive energy, quite a similar contrast was obtained for the image of total energy dissipation, that is, the area enclosed between the loading and unloading curves. The truth of the matter is that the total energy dissipation image is very much affected by the strength of adhesive force. In any case, we succeeded in clearly visualizing the differences of NR/IIR. Softer but more adhesive domains are IIR and the harder but less adhesive matrix is NR. Several rigid particles whose diameter is around 100 nm should be zinc oxide (ZnO) added for vulcanization.

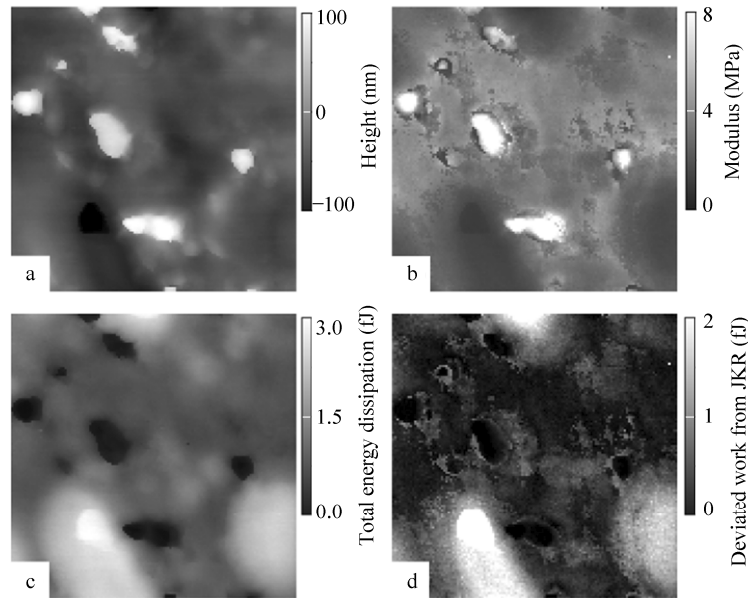


Fig. 8 Images of a NR/IIR blend derived from nano-palpation mapping with 128×128 force-distance curves: (a) apparent topographic, (b) Young's modulus, (c) total energy dissipation images and (d) the image of the deviated work from JKR theory

The scan size was $2.0 \mu\text{m}$.

However, while JKR curves fit well to the experimental data at NR region, they deviate largely at IIR region. Typical curves at NR matrix and IIR domain are shown in Fig. 9 as well as that of ZnO. It is natural to assume viscoelasticity caused the deviation at IIR. Thus we calculated the area encircled by the theoretical curve (solid grey line in Fig. 9) and experimental unloading data (open circles) of every force-distance curve and mapped the result onto two dimensional coordinate in Fig. 8(d). Note that two-point method only uses balance and maximum adhesion points for the calculation. The derived image shown in Fig. 8(d) clarifies the difference of viscoelasticity between NR and IIR. It gave larger value on IIR region while almost zero on the region of NR and ZnO. We may claim that the deviation mapping from elastic model can be an easy technique to visualize the distribution of viscoelasticity. This technique requires no further procedures or difficulty than conventional force-mapping measurement.

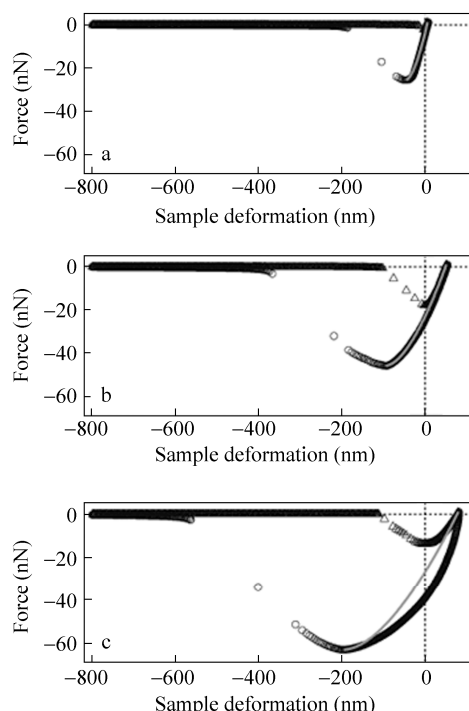


Fig. 9 Typical force-separation curves at (a) ZnO particle, (b) NR matrix and (c) IIR domains. The open triangles and circles are experimental data obtained during loading and unloading, respectively; The lines are theoretical curves based on JKR two-point method.

CONCLUSIONS

The nano-palpatation technique, *i.e.*, nanometer-scale elastic and viscoelastic measurements based on AFM, was introduced. It is demonstrated to be very useful in analyzing nanometer-scale materials properties for the surfaces and interfaces of various types of soft materials. It enables us to obtain not only structural information but also mechanical information about a material at the same place and at the same time. We also demonstrated the possibility to visualize viscoelastic property as the deviated work from the framework of elastic theory.

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