Polymer nanotechnology applied to polymeric nano-soft-materials

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Abstract.
We have been developing new techniques to evaluate polymer nano-alloys and nano-composites. This “nanotechnology” can be classified into nano-three dimensional (3D) measurement, nano-physical properties evaluation systems, and nano-spectroscopy. As for the nano-3D measurement, we developed polymer oriented energy-filtered 3D transmission electron microscopy. With this method, we can access important 3D structural and elemental information that cannot be obtainable from ordinary TEM. Nano-physical properties evaluation systems were also established by developing atomic force microscopy force-distance curve measurement. The distribution of mechanical properties such as Young’s modulus and adhesive energy was quantitatively obtained on high lateral resolution. These methods give new pieces of information unobtainable by the conventional techniques on polymer nanotechnology. Several results are shown here.

1. Introduction
In order to satisfy industrial demands for various purpose, vigorous research and development have been done on polymer blends and polymer composites. Recently the dispersion size of filled composite can be as small as on nanometer scale. However, the relationship between macroscopic physical properties and microscopic morphological structures was still obscure. In order to boost efficient development and promote creation of novel materials, it is important to develop techniques to evaluate nano-distribution directly. We categorized the required methods into three; nano-three dimensional (3D) measurement, nano-physical properties evaluation systems and nano-spectroscopy. We introduce the first two techniques in this paper.

Transmission electron microtomography (TEMT) is an emerging technique for observing real-space 3D images in nanoscale [1, 2]. Electron energy loss spectroscopy (EELS) is another important technology in transmission electron microscopy (TEM) that enables us to obtain element-mapped images [3]. With these two techniques together, it becomes possible to obtain elemental-mapped 3D images in materials. Such attempts have been carried out in “hard materials”, e.g. metal alloys [4], but few studies on “soft materials”, such as polymers, due to the severe electron beam damage to polymers. Most of the structural observations using EELS in polymer nanotechnology so far are limited to two-dimensional (2D) [5, 6]. Needless to
say, such loss of one of the three dimensions results in substantial drawback in the structural observations. The growing need for 3D elemental-mapping, i.e., combined TEMT and EELS (TEMT-EELS) has been apparent.

For the purpose of evaluating local physical properties, atomic force microscopy (AFM) has a great advantage. While AFM can capture surface morphology on nanometer-scale lateral resolution, it can detect interactive force which works between a sample and a probe. AFM is mostly used in intermittent contact mode in order to observe surface morphology and phase image was thought to be responses of mechanical properties. However, to derive some physical properties from a phase image is quite difficult [7]. On the other hand, force-distance curve measurement has an advantage that it can obtain quantitative mechanical properties such as Young’s modulus. A force mapping measurement is a method to measure force-distance curves at each point after dividing a sample surface into a grid. We combined force mapping measurement with force-distance curve analysis and succeeded in visualizing distribution of Young’s modulus on high lateral resolution [8, 9]. We show the recent progress where adhesion-conscious theory is applied.

2. Experimental

2.1. nano-3D measurement

A poly(sulfone-block-amide)(PSU-b-PA) (\(M_n = 1.5 \times 10^4, M_w = 5.3 \times 10^4\)) was used [6]. The sulfone block contains sulfur (\(\phi_{\text{PSU}}=0.54\)). A film specimen was prepared by casting 5 wt\% hexafluoroisopropanal solutions for 2 days at room temperature and then annealed at 195 °C under vacuum for 24 h. The obtained film specimen was ultramicrotomed to the ultrathin sections (thickness: 50 nm) and stained with RuO\(_4\) vapor for 5 minutes. TEM and TEMT images were taken using a JEOL JEM-2200FS microscope. EELS and TEMT-EELS images were taken by three-window method [3]. The electron dose has to reduce in order to suppress the electron damage during the TEMT-EELS experiments. In this experiment, relatively loose the energy resolution (±15 eV) was selected and the focus change due to the electron-energy change was determined prior to the TEMT-EELS experiments. The former allows us to use shorter exposure time and the latter to select appropriate focus without exposing excess electrons for determining the focus during the experiment. The total electron dose was 450 pA/cm\(^2\).

2.2. Nano-physical properties evaluation

Natural rubber (NR) vulcanizates were chosen as typical industrial materials. The recipe to obtain NR vulcanizates is shown in Table 1. The vulcanizate was cured at 145°C for 30 minutes and a sheet with the thickness of 1.0 mm was made. The crosslink density was measured by swelling it in toluene and calculated with Flory-Rehner equation. The density value was \(1.47 \times 10^{-5}\) mol/cm\(^3\). The average numbers of monomer units between crosslinks were 465. The NR sheet was then cut by a cryomicrotome at \(-180^\circ\)C to expose a flat surface.

| Table 1. Recipe for NR vulcanizates |
|-------------------------------------|
| NR | ZnO | stearic acid | accelerator\(^1\) | antioxidant\(^2\) | sulfur |
|-----|-----|-------------|-----------------|---------------|--------|
| 100 | 5.0 | 2.0        | 0.5             | 0.5           | 0.5    |

\(^1\) 2-mercaptobenzothiazole, \(^2\) Santflex 13 (Monsanto).

A Nanoscope V scanning probe microscope (Veeco Metrology Group, USA) with NP-1 wide short cantilevers made of silicone nitride (Nanoprobe, USA) was employed. Nanoscope V system
provides the derivation method of a spring constant of a cantilever from thermal noise, which Hutter et al. originally proposed [10]. The nominal value and calibrated value of spring constant was 0.58 and 0.12 N/m, respectively. The calibrated value was used in the following. We operated force mapping measurement with 50 nm of trigger deflection in air.

3. Results and Discussion

3.1. nano-3D measurement

Figure 1. (a) TEM image, (b) the sulfur map obtained by three-window method and (c) superimposed image of (a) and (b) for the RuO$_4$-stained PSU-b-PA. The bar shows 50 nm.

The 3D nano-structure of the PSU-b-PA was investigated by TEMT-EELS. The ultrathin sections of the RuO$_4$-stained PSU-b-PA was observed by TEM (Fig. 1(a)). The gray and bright area correspond to the RuO$_4$-stained PSU and PA microdomains, respectively. This image suggests that PSU-b-PA exhibited bicontinuous-like structure, as speculated in the previous study using the same PSU-b-PA block copolymer [6]. The dark small dots in the image are gold nanoparticles used later as fiducial points for the alignment of the tilt series [11] and three-window method. The 2D Fourier transformation of the TEM images was carried out, from which the domain spacing of the microphase separated structure was estimated to be ca. 27.2 nm. This spacing is in agreement with the result obtained separately by small-angle X-ray scattering measurements, i.e., ca. 30 nm [6]. In order to obtain the sulfur map of the PSU-b-PA, EELS was carried out at the same area as the TEM observation (Fig. 1(a)), which is demonstrated in Fig. 1(b). The yellow area corresponds to the area with high sulfur content. The sulfur map is superimposed on the TEM image (Fig. 1(a)) and shown in Fig. 1(c). It was found that the sulfur domain exactly overlaid on the gray ones, i.e., RuO$_4$-stained PSU microdomains, which ensures that EELS gives precise element specific map as expected. However, since the sulfur overlapped along the depth of the ultrathin section, the structural information along this direction is lost in the 2D sulfur map. In order to grasp the 3D sulfur distribution in the specimen, it is necessary to combine EELS with TEMT (TEMT-EELS).

The resulting reconstructed 3D sulfur map of the PSU-b-PA obtained by TEMT-EELS is shown in Fig. 2. The yellow phase corresponds to the microdomains with high sulfur content (and hence PSU microdomains). Z-axis corresponds to the optical axis of electron microscope and also to the depth direction of the ultrathin section. The sulfur distribution is continuous in all direction in the ultrathin section: It is clear from the 3D sulfur map that the PSU-b-PA exhibits the bicontinuous structure. The 3D sulfur map in the PSU block copolymer was distinguished by TEMT-EELS.

3.2. Nano-physical properties evaluation

Figure 3 shows a typical force-distance curve obtained on a NR vulcanizate. Force-distance curves give the relationship between the z-scanner displacement $Z$ and the cantilever deflection
Figure 2. The 3D sulfur map obtained by TEMT-EELS of unstained PSU-b-PA reconstructed by the simultaneous iterative reconstruction technique (SIRT) [12]. The box size is 200 nm × 200 nm × 35 nm. The yellow phase corresponds to the the area with high sulfur content.

d. Sample deformation δ is calculated by subtracting the cantilever deflection from the scanner displacement (δ = Z − d). On the other hand, applied load F is derived from the spring constant k and the deflection of the cantilever (F = kd). Figure 4 is force-deformation relationship derived from Figure 3 with these equations.

Figure 3. Typical force-distance curve on a NR vulcanizate. A dash line is on approaching, and a solid line retracting.

Figure 4. Force-deformation relationship derived from Figure 3. Crosshairs and circles are approaching and retracting experimental data, respectively, and a gray solid line is a calculated JKR curve.

There are several theoretical models which describe the mechanical contact between two bodies under external load [7]. Hertz theory was an old but basic theory. Derjaguin et al. (DMT) extended it and their limit equation of mechanical contact between an elastic plane and a solid sphere

\[ F = KR^{1/2}δ^{3/2} + F_0 \]  

was well used for its simplicity, where K, R and F_0 are elastic coefficient, tip radius and constant adhesive force, respectively. Assuming a probe is rigid and a sample is elastic, Young’s modulus E was given by the following equation

\[ E = \frac{3}{4}(1 − \nu^2)K \]

where E and \( \nu \) are Young’s modulus and Poission’s ratio of a sample, respectively. Our past report used it in water so as to constrain adhesion [8]. However, rubbery materials shows adhesion between cantilever, especially in air; for such condition, Hertz theory is inadequate [13].
Another theory extended by Johnson et al. (JKR) takes adhesion energy $w$ into consideration \[14\]. The theory is described as follows.

$$F = \frac{K}{R} a^3 - 3w\pi R - \sqrt{6w\pi RF + (3w\pi R)^2}$$ \hspace{1cm} (3)

$$\delta = \frac{a^2}{3R} + \frac{2F}{3aK}$$ \hspace{1cm} (4)

Because these equations are unable to be converted to an explicit function of $\delta$ and $F$, the least mean square curve fitting is not applicable. Therefore, we applied “two-point method” proposed by Sun \[15\]. In this method a JKR curve was drawn so as to cross the two typical points; one point is where the attractive force and repulsive force become equivalent ($((\delta_0, 0)$ in Figure 4), and another is where adhesive force becomes maximum ($((\delta_1, F_1)$ in Figure 4). Using these two points, JKR equations are converted to the following functions where $K$ and $w$ are explicitly represented:

$$K = \left(1 + \frac{16^{1/3}}{3}\right)^{3/2} \frac{F_1}{\sqrt{R(\delta_0 - \delta_1)^3}}$$ \hspace{1cm} (5)

$$w = \frac{-2F_1}{3\pi R}$$ \hspace{1cm} (6)

Thus, equations 2, 5 and 6 give $K$ and $w$ from a force-distance curve. Assuming $\nu = 0.5$ and $R = 20$ nm, the Young’s modulus and adhesive energy of the curve in Figure 4 were 0.74 MPa and 0.723 J/m$^2$, respectively. The derived curve is depicted with a gray solid line in Figure 4. On the other hand, equation 1 based on DMT theory gave Young’s modulus of 3.8 MPa. This mismatch was made by the inconsideration of adhesion in DMT theory \[13\]. Because of the jump-in adhesion the slope in Figure 4 became steep, thus the apparent modulus increased.

Constructing a result of a force mapping measurement onto a two-dimensional coordinate, distribution images of Young’s modulus and adhesive energy were clearly visualized. The result is shown in Figure 5. Both images were simultaneously obtained from one force mapping measurement. The z-directional color scale of the adhesive energy image is inverted for comparison with Young’s modulus image. Several grains whose sizes are around 1 $\mu$m were observed. Judging from an analogy in electron microscopy images, they seem to be made of ZnO. Comparing both images, obvious is a general relationship that softer area has strong adhesion. However, several deviations from the relationship were also observed. Figure 6 shows profiles of dotted line in Figure 5. While they have inverse relationship on 3–7 $\mu$m position, a hard area around 2 $\mu$m shows strong adhesion and weak adhesive area around 9 $\mu$m gives low modulus (Note that curve of adhesive energy is also inverted). It is because the origin of modulus and adhesion are not the same; adhesive energy is affected by chemical affinity but modulus not. Intermittent contact mode AFM or other method is incapable of distinguishing there differences. Force mapping measurement with JKR analysis only clarified these differences.

4. Conclusions
An example of advanced nano-3D measurement, combined TEMT and EELS (TEMT-EELS), has been given. After adjusting the energy resolution and the pre-determination of the focus change due to the electron-energy change during the EELS measurements, electron dose to the specimen was substantially reduced. The 3D sulfur map of a microphase-separated structure of a poly(sulfone-block-amide)(PSU-b-PA) was obtained using such low-dose TEMT-EELS. Bicontinuous morphology was clearly observed from the TEMT-EELS observation, which was only inferred in the previous study from the 2D TEM micrographs.

The combination of JKR analysis with force mapping measurement was shown for industrial rubber composites. Both Young’s modulus distribution and adhesive energy distribution were
Figure 5. Result of force mapping measurement and JKR analysis. (a) Young’s modulus distribution image. (b) Adhesive energy distribution image. The scan size was 10 µm and both images were obtained simultaneously. Note that the color bar of z scale in the adhesion image is inverted for comparison with the modulus image.

Figure 6. Section of a dotted line in Figure 5. (a) Young’s modulus. (b) Adhesion energy. Note that the y scale in the adhesion section is inverted for comparison with the modulus section.

obtained with high lateral resolution. Both images roughly have inverse relationship, but not precisely. It means that material properties of different origin were separately visualized by this measurement.

These methods give new information unobtainable by the conventional techniques on polymer nanotechnology.

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