Nanomechanical Properties Analysis on Polymer Blend Surfaces by Atomic Force Microscopy

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Introduction

Atomic force microcopy (AFM) contact and intermittent contact (tapping) modes are widely used to obtain topographic images of elastic samples such as polymers and biomaterials. In both contact and tapping modes samples are scanned over their surfaces with mechanical contact in a condition where deflection and amplitude, respectively, of a cantilever is kept constant by feedback loop. Therefore it can be said that topographic image obtained from these methods is inevitably affected by applied force.

AFM is also applicable to mechanical properties analysis of material surfaces. There are several reports in which force-distance curves measurement was employed and elastic properties were derived by analyzing experimental result as continuum mechanical problem. Force-distance curves also give us information at each sample indentation. Our group has focused on force-mapping methods—dividing sample surface into lattice, measuring force-distance curve at each of lattice point, and construct 2-dimensional Young's modulus image and so forth from analytic result of force-distance curve. We recently reported the application of this method on PS/PIB blends.[1] In this report we successfully reconstructed a topographic image in the condition where no force applied. We claim that rubbery regions deform much more than glassy regions, hence force-mapping method should be used to obtain accurate topographic image.

Experimental

Sample Preparation. Natural rubber (NR) and ethylene propylene diene elastmer (EPDM) were chosen as a model sample because both are in rubbery state at room temperature and it is known that their blends compose a phase-separated structure. NR/EPDM were dissolved in mutual solvent, toluene, in the composition of 5:5 and then the solution was spin-coated onto glass slides (1000 rpm, 1 min) to compose to obtain thin films of the polymer samples. The films were subsequently annealed at 100°C in vacuum for 3h, followed by gradual cooling to room temperature. NR/EPDM was immiscible at room temperature and had phase-separated structure.

AFM. A Nanoscope IV scanning probe microscope (Veeco Instruments) was employed. A TappingMode measurement was obtained using a commercial Si cantilever (MPP-11100, 300 kHz, Veeco Instruments), a force-volume measurement using commercial silicon nitride cantilever (wide short one of NP, Veeco Instruments). The spring constant of NP was derived to be 0.35 N/m (nominal value is 0.58 N/m) from thermal fluctuation spectroscopy.[2] To avoid adhesive and capillary force working between a cantilever and a surface, measurements were performed in distilled water.

Results and discussion

Tapping mode phase image of a NR/EPDM 50:50 blend film is shown in Figure 1. Though we can observe domain-matrix boundary, there are little difference observed between NR-rich regions and EPDM-rich regions. We speculate that this is because tapping speed is too high that both components act glassily.

Figure 2(a) and (b) are typical force-distance curves obtained on matrix and domain regions, respectively. Deducing contact point and using simple relation force-distance curves can be converted to force-deformation relationship (Figure 2(c), (d)). By adopting Hertz theory[3] between a elastic plane and a stiff conical tip on force-deformation curves, Young's modulus was derived from each force-distance curve (See Ref[1] for details). Figure 3 shows Young's modulus image of NR/EPDM thin film derived from this method. Force-distance curve measurement was performed at each 64 × 64 points for 10 × 10 μm, thus lateral resolution was about 150 nm. Young's modulus image shows obvious contrast between NR and EPDM, while phase image did not. Since macroscopic Young's modulus of EPDM is higher than that of NR, domain regions deduced to be EPDM-rich.

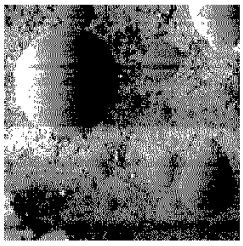

Figure 1. Tapping Mode phase image of a NR/EPDM 50:50 blend film cast on a glass plate (scan size: 10 μm). Though the domain-matrix structure is clearly observed, it is difficult to deduce which NR-rich domains are.

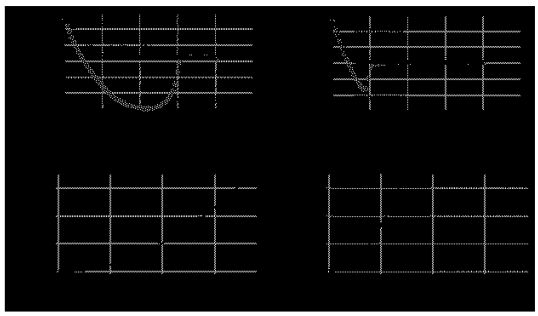

Figure 2. (a), (b) Typical force-distance curves on matrix region and domain region, respectively, of a NR/EPDM 50:50 blend film. (c), (d) Force-deformation relationships which were derived from (a) and (b), respectively(circles). The curve-fitting results (line) are also depicted.

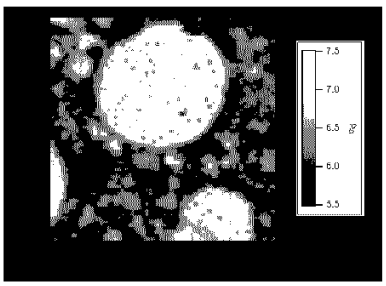

Figure 3. Log-scaled Young's modulus distribution image calculated from the results of force-mapping measurement on a NR/EPDM 50:50 blend film. The scan size is 10 μm. The trigger threshold is 50 nm. A force-distance curve is incorporated for each 64 × 64 pixels.

Conclusions

We succeeded in obtaining Young's modulus distribution image of rubbery/rubbery blend materials in sub-micrometer resolution. This image differentiated the mechanical properties which phase image could not. Here we adopted Hertz theory, which ignored adhesive force, for simplicity, but another theoretical model that take adhesion into account[4] is also adoptable in these material. We will also show recent theoretical extension of force-mapping measurement in the conference.

References

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