

## Observation of Carbon Nanotube/Elastomer Composites by Atomic Force Microscopy

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### Introduction

In recent years, it has been made clear that replacing  $\mu\text{m}$ -sized fine particles with nanoparticles in polymer composite systems gives great changes of physical properties. These composite systems are named as polymer nanocomposites. Because the size of an interface phase between a polymeric matrix and a composite material in polymer nanocomposite system nearly corresponds that of the composite material itself, the interface phase would play an important role to determine the mechanical properties of polymer nanocomposite systems.

Multi-wall carbon nanotubes (MWCNT) has possibility to become a promising filler in polymer matrices, because it has an extraordinary high strength and elastic modulus. Noguchi *et al.* reported that the elastic modulus of MWCNTs/natural rubber (NR) composite amounts to 20 times as high as that of HAF-carbon black (CB, mean particle size 28 nm)/NR [1]. However, its unusual enhancement could be interpreted by conventional theories such as Halpin-Tsai [2], [3] or Guth [4] equations. Thus, we paid our attention to the interface phase around CNTs in NR matrices to reveal how the elastic modulus improves.

In this study, atomic force microscope (AFM) [5] was used as the tool to investigate sectioned surfaces and mechanical properties of CNTs/NR composites. AFM enabled us to observe their surface topography in nanometer-scale and to simultaneously estimate their mechanical properties. Nukaga *et al.* reported that it was possible to reconstruct a real height image, a sample deformation image and an elastic modulus image of the sample with analysis of the force-distance curve using Hertz theory [6]. We investigated the nanorheological property of CNT/NR nanocomposite using AFM.

### Experimental

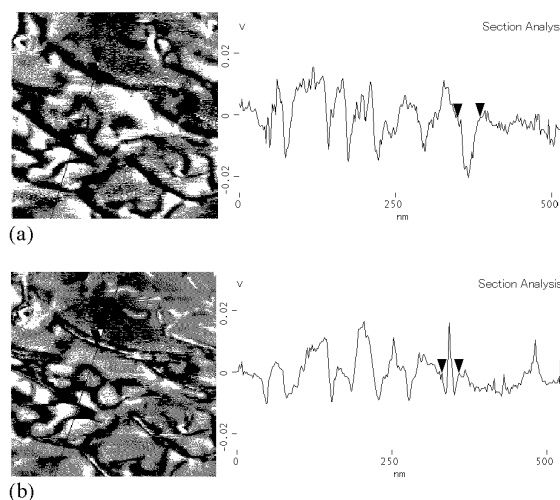
**CNT/NR composites.** NR (CV-60) was used as an elastomer matrix. As a filler, MWNT having arithmetic mean diameter of 13 nm (CNT13, IJIN Nanotech Co. Ltd.) was used. The respective fillers were incorporated by 2.5, 10 parts against 100 parts of rubber matrix (phr). As a crosslinking agent, bi-functional peroxide (PO, 1,3-Bis(7-butyl) peroxisopropyl)benzene) or sulfur was added respectively. The specimens were prepared as follows; on a six-inch two-roll mill, the respective elastomers were placed and rolled upon themselves, and the required amounts of respective fillers were mixed with the elastomers. With the mixtures temporarily removed, the nip was tightened to 0.3 mm. The respective mixtures were then replaced and subjected to 10 passes through the mill in order to apply a strong shear stress. For the preparation of crosslinked specimen sheets, the compounds were sheeted into slabs of 1.2 mm and cured by compression moulding. The CNT/NR composites prepared by the above process were cut to obtain smooth surfaces by ultra-microtome (REICHERT FCS, Leica Co. Ltd.) as AFM specimens. Thin small pieces were subjected to the observation by transmission electron microscope to check the structure and dispersion condition of CNTs.

**AFM.** All AFM experiments were performed by Nanoscope IV (Veeco Metrology Group, USA). E-scanner (max scan range of 10  $\mu\text{m}$  to x-y directions and 2.5  $\mu\text{m}$  to z direction) was used. For force modulation mode, MPP-21100-10 (Veeco Metrology Group, USA) was used as an appropriate cantilever. Its resonant frequency was 60-90 kHz and the nominal value of its spring constant was about 3 N/m. The force modulation vibration was generated by a bimorph attached at the cantilever holder. The resonant frequency of the bimorph was 8.35 kHz. The experiments were performed under ambient conditions. In contrast, NP-1 (Nanoprobe, USA) was used as an appropriate cantilever for force-distance curve measurements, which had a value of 0.11-0.58 N/m for the spring constant. The experiments were

performed under ambient conditions or in distilled water to reduce adhesive interaction.

### Results and discussion

Figure 1 shows the force modulation amplitude images and their section analyses of 2.5 phr CNT/NR composite. The scan size was 1  $\mu\text{m}$ .



**Figure 1.** The force modulation amplitude images (left) and the cross-sectional analyses of along the solid line (right) with lift height of (a)  $-15\text{ nm}$  and (b)  $-20\text{ nm}$  for 2.5 phr CNT/NR composite.

In Figure 1(a), the slender structures which had lower value of amplitude than surroundings were seen. The distance between two triangles was estimated to be about 30 nm, which was similar to the diameter of the CNTs. We never observed such a structure with pure NR matrix. For these reasons, we expected that the slender structures might be CNTs. However, the whole slender structure proved to show lower amplitude than NR matrix. This area was recognized as low elastic modulus part. Since CNT should have higher elastic modulus than NR matrix the slender structure should not be CNT itself.

After lift height was lowered until  $-20\text{ nm}$ , it caused a dramatic change of the amplitude image. The image obtained by this process was shown in Figure 1(b). We could recognize there existed two different contrasts in the slender structure. It meant that there were two areas with different mechanical properties. The outer side in the slender structure gave lower amplitude like Figure 1(a), while the inner side, gave higher amplitude than both NR matrix and the outer side. Interpreting force modulation amplitude, the inner and outer sides in the structure had higher and lower elastic moduli, respectively. This result was also obtained with the sample cured by sulfur. We might be able to conclude that there were two different portions in the slender structure, CNT itself and soft interface phase. The result of force-curve measurements also agreed with this conclusion.

### Conclusion

In CNT/NR composite system, the interface phase around CNTs indicated lower elastic modulus than NR matrix that was revealed by force modulation amplitude image. We speculated that the interface phase between NR and CNT was effected on the mechanical properties of the CNT/NR nanocomposite.

### References

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