How to Detect Viscoelastic Properties of Polymeric Materials by Dynamic Atomic Force Microscopy

Ken Nakajima,*[,1] *So Fujinami*,[1] *Toshio Nishi*[1]

[1]Department of Organic & Polymeric Materials, Tokyo Institute of Technology, Tokyo, 152-8552 Japan
knakaji@polymer.titech.ac.jp

Introduction

There are several types of dynamic atomic force microscopy (AFM) such as *so-called* tapping-mode, force modulation-mode and *so on*. These modes are commonly cooperated by phase contrast imaging techniques, which were interpreted as elastic contrast by mistake in the past and are nowadays regarded as the representation of energy dissipative processes. However, as theoretically reported by Tamayo *et al.* [1], the situation is not so simple when the strong adhesive interaction is involved even if it is purely energetic contribution. Furthermore, elastic and viscous contributions are not easily divided in the case of polymeric systems because the systems inherently possess viscoelastic nature. Thus, the interpretation of image contrast for them must be very carefully treated. In this study, we will demonstrate how such contrast mechanisms are complicated. If possible, we would like to point out some guidelines for obtaining better understanding to them.

Experimental

We adopt two polymer blend systems as model samples for the investigation of the above-mentioned story. Polystyrene (PS)/poly-isobutyrene (PIB) immiscible blend can be regarded as the first candidate because they have very different glass-transition temperature, T_g, where PS (T_g = 100°C) is in a glassy-state, while PIB (T_g = -76°C) is in a rubbery-state at room temperature. Another candidate is PS/ poly (methyl methacrylate) (PMMA) miscible system. Since PMMA has T_g of 120°C, their mechanical properties are quite similar to each other.

Results and discussion

Firstly, we performed the force-distance curve analyses in the contact-mode, tapping-mode and force-modulation-mode operations in order to give some idea for polymeric materials using PS/PIB blend system. For the latter two cases, amplitude, phase and tapping-mode deflection signals were plotted against tip-sample distance (data not shown). Then, we demonstrated more quantitative analysis using several classical contact mechanics such as Hertzian contact, where we could reproduce "real height" images together with elastic modulus images by considering the deformation of samples interacting with probe tips (data not shown) [2, 3].

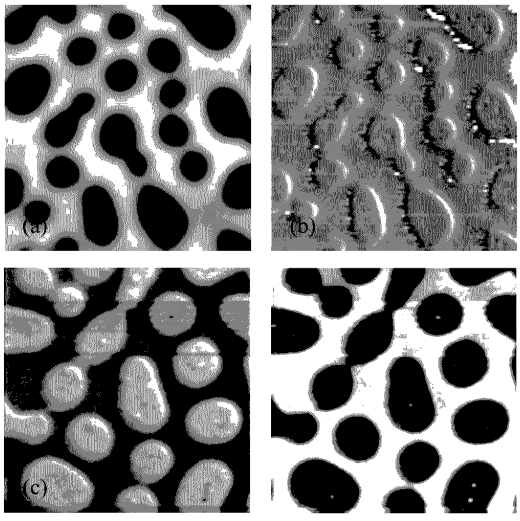

Figure 1. (a) tapping-mode height image of PS/PMMA blend, (b) the corresponding phase contrast image, and (c) & (d) force modulation amplitude and phase images.

Another topic was related to PS/PMMA blend system. Its phase-separated structure was investigated by tapping and force modulation modes as shown in Figure 1. According to the time-temperature superposition principle, the behavior of polymeric systems varied depending on the speed or frequency of stimulation. When the frequency was too high in terms of their relaxation times (tapping-mode with 300 kHz), subtle difference in mechanical property could not be observed as shown in Figure 1(b) (tapping-mode phase contrast), while sufficiently slower frequency (force modulation with less than 10 kHz) revealed such difference as shown in Figure 1(c&d). However, the successful discrimination could not be directly interpreted as the result of the detection of viscoelastic difference because PS and PMMA had different surface energy, which could also contribute to amplitude and phase changes. We investigated force-distance curve for PS/PMMA blend sample during force-modulation-mode operation and confirmed the mechanism of its image contrast was largely affected by the difference in adhesive interaction.

To solve the problem, we performed scanning viscoelastic microscopy with much slower excitation (around 0.5 kHz) as shown in Figure 2. The frequency response was also measured. Then, we could observe some contrast in amplitude image, while phase difference was not clear. We tried to understand this reason using dissipation map. The detailed discussion will be made at the site.

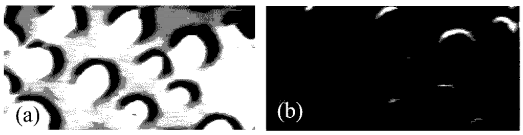

Figure 2. Scanning viscoelastic microscopy performed on PS/PMMA, (a) amplitude and (b) phase images obtained for 0.5 kHz perturbation.

Conclusions

We performed several dynamic AFM on PS/PIB and PS/PMMA blend systems. The following could be conclusive remarks:

1. Frequency sweep was indispensable to complement temperature control.
2. Phase shift or energy dissipation, related to sample viscosity, should appear at narrow frequency range.
3. Amplitude change must be investigated together with phase shift for soft material systems.

References

[1] Tamayo, J.; García, R. *Appl. Phys. Lett.* **1997**, *71*, 2394.
[2] Nukaga, H.; Fujinami, S.; Watabe, H.; Nakajima, K.; Nishi, T. *Jpn. J. Appl. Phys.*, **2005**, *44*, 5425.
[3] Nakajima, K.; Fujinami, S.; Nukaga, H.; Watabe, H.; Kitano, H.; Ohno, N.; Endo, K.; Kaneko, M.; Nishi, T. *Jpn. J. Polym. Sci. Technol.*, **2005**, *62*, 476.