

AFM을 이용한 고분자 나노 구조의 계면 현상 및 특성

박영준, 김중현

서울시 서대문구 신촌동 연세대학교 화학공학과 기능성 초미립자 공정 연구실

Interfacial & Surface Properties of Polymeric Nano-Structure Characterized with Atomic Force Microscopy

Young-Jun Park, Jung-Hyun Kim,

Nanosphere Process and Technology Laboratory, Department of Chemical Engineering, Yonsei University, Seoul 120-749, Korea

서론

The chemical nature of surfaces plays an important role in catalysis, compatibility, chemical recognition, semiconductor devices, adhesion and the chemical modification of surfaces [1], The understanding of these phenomena relies on knowledge about the interaction between interfacial and surface properties at the molecular level.

Several techniques to probe the interfacial interaction between molecules or molecular assemblies have been developed, such as the surface force apparatus, optical tweezers, and atomic force microscopy (AFM) [2~4]. The AFM has the capabilities of its combination of surface imaging with high resolution and ability to measure force interactions between molecules.

Surface imaging by conventional contact-mode AFM provides only topography images and does not inform about the chemical nature of the surfaces [5]. The friction mode force microscopy can be used to image chemically distinct areas [6], but the exact relationship between friction force and chemical functionality may not exist. Another technique to introducing chemical specificity into conventional AFM to provide a force interaction between the tip and the surface groups by modifying standard AFM probes with specific functionalities [7]. The chemical functionality on a surface can be probed via a specific chemical interactions (e.g. hydrogen bonding, coulombic or pi-stacking interaction) between scanning probe (X) and the surface which bears the chemical functionality of

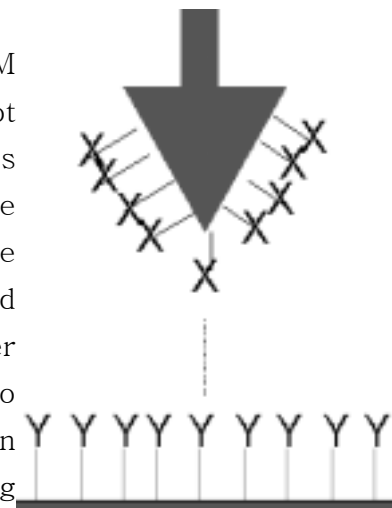


Fig. 1. Schematic drawing of a chemically modified AFM tip with functional groups (X), which exhibit a specific interaction with functional groups of interest (Y) on the sample surface.

interest (Y) as shown in Fig. 1. This approach requires: (a) a versatile and simple method to change the tip functionality, (b) strong (covalent) binding of the molecules to the tip, (c) a mechanically stable layer and (d) a chemically stable layer (organic liquids, pH etc.).

Herein, we discuss the concept of the chemically modified AFM for friction, adhesion, chemical imaging and monitoring of chemical reactions [8,9]. The model system consists of tips and model substrates coated with self-assembling monolayers. The specific interactions between uncharged/charged functional groups could be interpreted in terms of the Johnson-Kendall-Robers theory (JKR) of adhesion mechanics. Friction force measurements constitute the basis for the chemical imaging which is demonstrated on patterned surfaces using the micro-contact printing technique. The ability of chemically modified AFM to chemically image features down to the nanometer scale using a microphase-separated block copolymer as a patterned model substrate.

본론

A substrate with self-assembled monolayers can be used with either OH or COOH terminal groups to study the surface chemical reactions, During the reaction of butyl isocyanate with the OH-terminated SAM, the end groups are converted into a urethane link with the butyl as the end group of the SAM. The reaction conversion can be investigated with an amide-functionalized AFM probe via force-distance profiles, from which the adhesion forces were evaluated. Since the amide groups on the AFM probe can form strong hydrogen bonds with an OH-functional surface, a large adhesion force between tip and sample is expected. During the reaction of butyl isocyanate with the OH-groups, the end groups of the AFMs will change from alcohol groups to methyl groups. The resulting CONH₂-CH₃ interactions are much weaker (purely van der Waals forces) than the CONH₂-OH interactions (van der Waals and hydrogen bonding), leading to a decrease in adhesion force. From the measured changes in the adhesion forces, the local chemical composition and the reaction conversion of a chemical surface modification can be determined on a microscopic scale. The magnitude of the adhesion force is directly proportional to the magnitude of the friction force. In this way, a chemical map of the distribution of reacted (and unreacted) surface functional groups during a reaction can be obtained. This chemical mapping of the functional group distribution is demonstrated by the chemically specific lateral

force imaging of a pattern of CH_3/COOH regions of self-assembled monolayers which have reacted with butyl isocyanate in the presence of the catalyst. For the CH_3/COOH pattern, a moderate frictional contrast can be seen before the reaction between the CH_3 squares (dark, low friction) and the reactive COOH surroundings (bright, high friction)[7]. During the reaction, the acid surfaces change into methyl-terminated surfaces, leading to a diminishing of the frictional contrast. After 6 h the reaction is assumed to be complete, since the acid regions of the initial surface have approached the friction of the methyl regions and frictional contrast is no longer detectable. In this way, differences in the surface functional group distribution can be imaged during a reaction. No differences in frictional force can be seen within the reacted acid regions at the micron scale, indicating a homogeneous conversion across the surface. (Fig. 2)

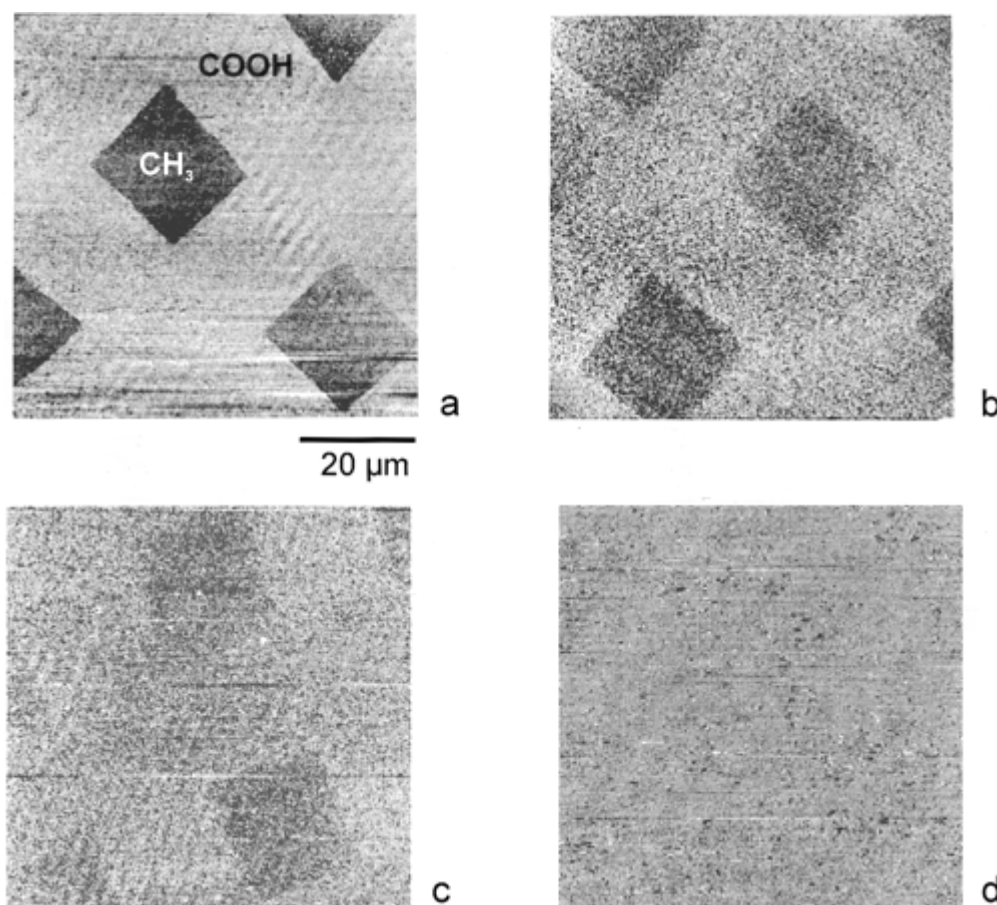


Fig 2. Friction force images of CH_3/COOH patterns before and after the reaction with butyl isocyanate. Bright (dark) areas represent high (low) friction. The disappearance of contrast is observed when the acid surface changes into a methyl-terminated surface. (a) Before reaction and after (b) 30 min, (c) 90 min, and (d) 360 min.

결론

One can determine the local functional group distribution and the reaction conversions of a surface modification reaction on a microscopic scale using AFM with chemical specificity. Furthermore, with chemically specific lateral force imaging, mapping of the distribution of reacted (and unreacted) functional groups on a microscopic scale during the reaction process can be possible.

참고문헌

- [1] J. N. Israelachvili, Intermolecular & Surface Forces: Academic Press: New York, 1992.
- [2] J. N. Israelachvili, J. Phys. Chem., 95, 10736, 1991.
- [3] T. Perkins et al., Science, 264, 819, 1994.
- [4] Y. J. Park et al., Langmuir, 14, 5419, 1998.
- [5] Y. J. Park et al., Colloids and Surfaces A, 153, 583, 1999
- [6] C. M. Mate et al., Phys. Rev. Lett, 59, 1942, 1987.
- [7] E. W. van der Vegte et al., Lagmuir, 13, 4939, 1997.
- [8] A. Noy et al., J. Am. Chem. Soc., 117, 7943, 1995.
- [9] S. Alari et al., Langmuir, 12, 854, 1996.