Direct observation of the morphology and peeling behavior of poly(vinyl alcohol) derivatives in water by scanning probe microscopy

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The morphology and peeling behavior of poly(vinyl alcohol) (PVA) derivatives in water is investigated. The uneven surface is observed through the tapping mode of scanning probe microscopy; it originates from PVA molecules adsorbed on the solid surface. The force curve shows an extension, which results in PVA peeling. The extension agrees well with the worm-like chain model. The persistence length of all PVA derivatives used in this study approximates the 2 C–C bonds (0.31 nm). The distribution of the contour length is plotted for each molecule based on fifty peeling tests. It shows that the conformation of PVA derivatives adsorbed on the solid surface reflects that of PVA derivatives in an aqueous solvent. These results indicate that the slight difference of functional groups affects the flexibility of the molecule and the adsorption behavior onto the solid surface is different.

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Poly(vinyl alcohol) (PVA) has a relatively simple chemical structure and is a water-soluble synthetic polymer. Many types of PVA derivatives have been synthesized for various such as papermaking, textiles, coatings, stabilizing colloids as well as for medical applications because they exhibit excellent bulk or gel properties.¹–³ Other important PVA applications include a wet-molding binder, which is used in ceramics. In recent years, the preparation of ultra-small high-spec multi-layer ceramic capacitor (MLCC) has been investigated, as a result of the huge demand for small electronic devices. One of the key technologies for preparing the present MLCC is wet molding of nanometer-sized electronic ceramic particles. Decades ago, the paste for wet molding was generally characterized by rheological properties.⁴,⁵ At that time, the micrometer-sized ceramics particles were used, whose molecular size was significantly larger than that of the PVA binder. However, now, it is no longer possible to ignore the size of the PVA since nanometer-sized particles can be manipulated.⁶ The adsorption and peeling properties onto the oxide solid surface also attracted attention from the industry.

The colloidal probe technique for scanning probe microscopy (SPM) is useful for analyzing the behavior of polymer additives in solvents⁶–¹² because it can realize direct measurement of the mechanical properties of polymers with piconewton sensitivity and subnanometer accuracy.¹³,¹⁴ Carboxymethylcellulose,⁶ polyacrylic acid,⁷ methylcellulose,⁸ ethylene oxide,⁹ polyethylenimine,¹⁰ and poly(ammonium acrylate)¹¹,¹² are rigorously investigated with regard to the mechanical properties of the molecules. In addition, measurements of PVA with 98% saponification in pH 3–10 aqueous solutions indicate that PVA depends on pH.¹⁵ Moreover, the PVA peeling properties are correlated with the microstructure of the slurries. And PVA is used for these application at natural pH (5–7). Therefore, the conformation should be understood near this value. In this study, the adsorption and peeling behavior of PVA derivatives in an aqueous solvent are observed by SPM.

PVA and PVA derivatives (average degree of polymerization: 2000; The Nippon Synthetic Chemical Industry Co., Ltd., Osaka, Japan), a fused SiO₂ glass (ES, Tosoh Corporation, Tokyo, Japan), and SiO₂ beads (HPS-2000, Toagosei Co., Ltd., Tokyo, Japan) were used in this study.
The PVA was 98 mol % hydrolyzed, and 2 mol % acetate groups remained (PVA 98%). The PVA derivatives are listed in Table 1. Ion-exchanged purified water was distilled using a water purifier (Auto still, Model WG-250; Yamato Scientific Co. Ltd., Tokyo, Japan). PVA or PVA derivatives were dissolved in ion-exchanged purified water to a concentration of 10 µmol/L. The pH of the solutions was approximately 6 (see supporting information Fig. S1). The surface morphology was observed using tapping-mode SPM (SPM-9700; Shimadzu, Kyoto, Japan) with an attachment to measure in PVA aqueous solution and a Si cantilever (OMCL-AC160TS-C2; Olympus Co., Tokyo, Japan). The SiO2 colloidal probes were prepared from SiO2 beads with a particle size of approximately 2 µm (HPS-2000, Toagosei Co., Ltd., Tokyo, Japan), tipless triangle cantilevers (PNP-TR-TL-50; Nanoworld AG, Switzerland), and epoxy glue (Araldite #1600; Showa Highpolymer Co. Ltd., Tokyo, Japan) using a micromanipulator (Model M331; Suruga Seiki Co. Ltd., Shizuoka, Japan). The obtained cantilever is shown in supporting information (Fig. S2). The spring constant was 0.08 N/m. SPM measurements were conducted based on the previously reported methodology. A fused SiO2 glass was cut into approximately 2 × 2 cm² plates before cleaning with acetone and ethanol for 15 min. After drying, they were immersed in an O3 atmosphere at room temperature for 15 min to remove organics. Force curve measurements were performed using a SPM (JSPM-5200; JEOL Ltd., Tokyo, Japan). The SiO2 colloidal probes and one fused SiO2 glass were set up as described in a previous report for measurements in a liquid. The obtained raw data were converted into force-distance (separation between the probe and surface) curves.

Figure 1 shows the SPM image of the SiO2 substrate in the PVA aqueous solution after soaking into the same solution for one day. The observed height is uneven by approximately 3 nm. These bumps are observed in everywhere of the substrate. In addition, an unevenness of approximately 10 nm is noted. However, the substrate has a substantially uniform structure; 10 nm of unevenness is observed for approximately every 60 nm. Both 3- and 10-nm unevenness originate from the adsorbed PVA molecules on the substrate at multiple points. The peeling behavior of this molecule is measured through the colloidal probe method. The diameter of the colloid used in this study is approximately 2 µm. This size is selected from the relationship between the curvature of the colloid and the height of the unevenness, when the colloid contacts the substrate.

Figure 2 shows the retractive force curve measured using the SPM colloidal probe method in the 0.1 mass % aqueous solutions listed in Table 1. In general, the data

| Table 1. PVA derivatives used in this study |
| name | Functional group [%] |
|  | -OH | -OCOCH3 | -OCOCH2COCH3 | -COONa |
| PVA (98%) | 98 | 2 | 0 | 0 |
| PVA (88%) | 88 | 12 | 0 | 0 |
| Acetoacetyl | 93 | 2 | 5 | 0 |
| COONa | 93 | 2 | 0 | 5 |

![Image](https://example.com/image1.png)  
Fig. 1. SPM image of the SiO2 substrate in the PVA aqueous solution.
shown refer to 50 individual measurements at different points. In each molecule, extensions are observed at 10–520 nm distances. Moreover, several extensions appear in most curves. It is considered that the point, at which the polymer chain adsorbs to the tip, is located randomly along the polymer chain. Based on this assumption, the extension to the structure of the molecule was calculated using the worm-like chain (WLC) model. The relationship between force $F$ and the extension of the polymer chain $x$ is given by the following formula:

$$F = \frac{kT}{p} \left[ \frac{1}{2} \left( 1 - \frac{x}{L} \right)^{-2} - \frac{1}{4} + \frac{x}{L} \right],$$

(1)

where $p$, $L$, $k$, and $T$ are the persistence length, the contour length of the polymer chain, the Boltzmann constant, and the temperature, respectively. The persistence length corresponds to the smallest unit of the molecule bent. The contour length is the maximum end-to-end distance of a linear polymer chain. Almost all of the extensions fitted Eq. (1) as shown red lines in Fig. 2. It indicates that they may be present alone, fitting the WLC model. In this case, the persistence length in all the extensions is approximately 0.31 nm. It is considered that this length is derived from the molecular structure.

Furthermore, the structure of the PVA molecules is subsequently studied through the DFT technique using the model compounds, where 1,3,5-hexanetriol was introduced instead of the PVA, for the calculations. A restricted hybrid nonlocal density functional, B3LYP $^{20}$ with the 6-311++G(d,p) basis set $^{21-26}$ was used for the calculations, which were conducted using the Gaussian 09 program. The length of C–C bond in the main chain is approximately 0.152 nm (Fig. S3). Similarly, the length of the C–C bonds in all of the PVA derivatives were calculated to approximately 0.152 nm. We hypothesize that the persistence lengths of all of the PVA derivatives used in this study correspond to 2 C–C bonds. Meanwhile, the effect of the different functional groups on the contour length is not yet clarified. Therefore, we attempt to determine the contour length distribution through a new analysis.

First, the force curves of each molecule are measured 50 times each. All obtained extensions are fitted to Eq. (1) to determine the contour length. The persistence length is maintained constant at 0.31 nm. Then, the distribution curve is obtained by integrating the calculated contour length. The resulting graphs appear in Fig. 3. The total number of COONa molecules is 47. This is derived from the fact that an extension is not observed in nearly half measurement. The solution used for the measurement is approximately pH 6.5, independent of the concentration. The zeta potential of both the substrate and the colloid probe is negative below a pH of 6.5 (Fig. S4).
distribution curves are produced in these cases. In this case, the conformations. The differences in flexibility of the molecule, and the adsorption behavior onto the solid surface is different.

References

1) C. A. Finch, “Polyvinyl Alcohol” Wiley, New York (1983).
2) M. I. Baker, S. P. Walsh, Z. Schwartz and B. D. Boyan, J. Biomed. Mater. Res. B, 100B, 1451–1457 (2012).
3) E. Marin, J. Rojas and Y. Ciro, J. Pharm. Pharmacol., 8, 674–684 (2014).
4) N. Özkan, C. Oysu, B. J. Briscoe and I. Aydin, J. Eur. Ceram. Soc., 19, 2883–2891 (1999).
5) T. Isobe, Y. Hotta and K. Watari, J. Am. Ceram. Soc., 90, 3720–3724 (2007).
6) A. Scherer, C. Zhou, J. Michaelis, C. Brauchle and A. Zumbusch, Macromolecules, 38, 9821–9825 (2005).
7) S. Biggs, Langmuir, 11, 156–162 (1995).
8) H. Yilmaz, K. Sato, K. Sato, Y. Hotta and K. Watari, J. Am. Ceram. Soc., 94, 3761–3767 (2011).
9) A. Kauppi, K. M. Andersson and L. Bergström, Cement Concrete Res., 35, 133–140 (2005).
10) T. Kakui, T. Miyauchi and H. Kamiya, J. Eur. Ceram. Soc., 25, 655–661 (2005).
11) T. Isobe, Y. Nakano, Y. Kameshima, A. Nakajima and K. Okada, Chem. Lett., 39, 1275–1276 (2005).
12) T. Isobe, Y. Nakano, Y. Kameshima, A. Nakajima and K. Okada, Appl. Surf. Sci., 255, 8710–8713 (2008).
13) M. Rief, F. Oesterhelt, B. Heymann and H. E. Gaub, Science, 275, 1295–1297 (1997).
14) M. Rief, M. Gautel, F. Oesterhelt, J. M. Fernandez and H. E. Gaub, Science, 276, 1109–1112 (1997).
15) T. Isobe, M. Nakasone, K. Nakazono, S. Matsushita and A. Nakajima, Ceram. Int., 39, 3857–3864 (2013).
16) T. Isobe, Y. Nakagawa, M. Hayashi, S. Matsushita and A. Nakajima, Colloid. Surface. A, 396, 233–237 (2012).
17) J. F. Marko and E. D. Siggia, Macromolecules, 28, 8759–8770 (1995).
18) C. Bustamante, J. F. Marko and E. D. Siggia, Science, 265, 1599–1600 (1994).
19) H. Li, W. Zhang, W. Xu and X. Zhang, Macromolecules, 33, 465–469 (2000).
20) A. D. Becke, J. Chem. Phys., 98, 5648–5652 (1993).
21) R. Ditchfield, W. J. Hehre and J. A. Pople, J. Chem. Phys., 54, 724–728 (1971).
22) W. J. Hehre, R. Ditchfield and J. A. Pople, J. Chem. Phys., 56, 2257–2261 (1972).
23) M. M. Francel, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, J. Chem. Phys., 77, 3654–3665 (1982).
24) M. J. Frisch, J. A. Pople and J. S. Binkley, J. Chem. Phys., 80, 3265–3269 (1984).
25) P. C. Hariharan and J. A. Pople, Theor. Chim. Acta, 28, 213–222 (1973).
26) T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. R. Schleyer, J. Comput. Chem., 4, 294–301 (1983).