DOI: 10.1002/masy.200850414

Effect of Heat Treatment Temperature on Surface Topography and Hydrophobicity of Polydimethylsiloxane/Titanium Oxide Hybrid Films

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Summary: Hydrophobic thin films of polydimethylsiloxane (PDMS) - titamium (hydrous) oxide hybrid material were deposited on glass substrate by dip coating from the precursor containing hydroxyl-terminated PDMS and titanium tetraisopropoxide (TIP), as well as small amounts of water and ethyl acetoacetate. Film's hydrophobicity was evaluated by performing contact angle measurement, while surface topography was analyzed by using an atomic force microscope (AFM). Effects of heat treatment temperature and TIP:PDMS ratio on film's hydrophobicity are described.

Keywords: atomic force microscopy; hydrophobic; polydimethylsiloxane; thin film

Introduction

Many surfaces in nature are highly hydrophobic and exhibit self-cleaning property.[1] Examples include the wings of butterflies and the leaves of some plants such as cabbage, Indian cress and lotus which is the best known superhydrophobic self-cleaning surface. Electron microscopy study of the surface of lotus leaves shows protruding nubs of about 20–40 μm apart, and the whole surface is covered with a smaller scale rough surface of waxy substance.

Hydrophobic surfaces have been fabricated by mimicking surface characteristics found in such plant leaves. The hydrophobic coatings are expected to be new materials for practical applications such as anti-wetting, anti-snow-adherence and friction reduction. Controlling and modifying wetting ability of the surfaces have been investigated to achieve superhydrophobic characteristics. Water repellent coatings have been achieved by different methods using hydrophobic additives, such as alkyl thiols, long-chain alkyl silane (C8-C12), fluoroalkylsilanes or polydimethylsiloxane (PDMS). Extensive studies focused on hybrid coating prepared from the PDMS and oxide component of such metals as Al (III), Ti (IV), Zr (IV), Nb (V) and Ta (V).[2–6] The PDMS has been used as hydrophobic constituent because of its low surface energy of 16–21 $\mathrm{mN \cdot m^{-1}}$. In addition, the PDMS-based hybrid films have been coated onto several transparent substrates due to their good optical transparency.

In this research, the hydrophobic PDMS-based hybrid films were deposited on glass surface from hydroxyl-terminated PDMS and titanium tetraisopropoxide (TIP) prepared by using a sol-gel method. The films were heat-treated for up to 200 °C to investigate heating effect on the film's hydrophobicity as well as to evaluate their thermal stability. In some experiment, the PDMS was added to the TIP solution at various ratios to study the effect of PDMS:TIP ratio on the film's hydrophobicity.

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Experimental Part

The hydrophobic hybrid films were deposited on glass substrates which were cleaned by ultrasonication in water and acetone, respectively. The cleaned substrates were dried in the oven before coating. Precursor solution for hydrophobic film coating was prepared by dissolving TIP (98%, Merck) in 1-propanol (99%, Fisher scientific) and stabilized by addition of ethyl acetoacetate (EAcAc, 98%, Merck). Then, the PDMS (MW of 4392, Aldrich) dissolved in 1-propanol was added into the TIP solution having TIP: PDMS molar ratios of 1.0: 0.5, 1.0:1.0, 1.0:1.5 and 1.0:2.0. A predetermined amount of de-ionized water was added into the resulting mixture to hydrolyze the TIP to form titanium hydrous oxide compound. The resulting solutions were kept at room temperature for 1 or 2 days. Film deposition on glass substrate was performed by using a dip coater operated at a withdrawal speed of 0.01 $\mathrm{mm \cdot sec^{-1}}$. The resulting films were heat-treated at 60, 100 and 200 °C for 2 h in ambient air to investigate the effect of heat treatment on films' hydrophobicity. Furthermore, the effect of TIP:PDMS ratios to hydrophobicity was also investigated.

The film's hydrophobicity was measured at room temperature by using a contact angle goniometer. The measurements were repeated at least five times at different locations on the film's surface. Surface topography was analyzed by using an atomic force microscope (AFM) performed in a non-contact mode. Thermal property was studied by using a thermogravimetric analysis (TGA) performed in the temperature range of room temperature to 600 °C at a heating rate of 10 $\mathrm{°C \cdot min^{-1}}$ in nitrogen atmosphere.

Results and Discussion

Figure 1 shows the TGA profile of the prepared hybrid film. There was essentially no weight loss below 100 °C above which two distinct weight losses were observed. The first loss of 38% was in the temperature range of 200–400 °C while the second loss of 54% was in the temperature range of 400–550 °C. The two weight losses were attributed to decomposition of organic constituent in the TIP and degradation of the PDMS, respectively.[7–8] Based on this thermal result, the film was heat-treated to only 200 °C.

Figure 2 shows AFM topological images of the films containing TIP:PDMS ratio of 1.0:1.5 heat-treated at 60, 100 and 200 °C, respectively. The precursor solution was aged for 1 day before deposition. The films treated at 60 and 100 °C had similar topological feature that they consisted of fine protrusions (dimension of ~50–100 nm) and had surface roughness (R_a) of 1.2 nm and 3.0 nm, respectively. The two films had water contact angle of ~100 degree. Some bright features, ~0.3–0.5 μ in size, which might be titanium (hydrous) oxide particles were also observed. The film heated at

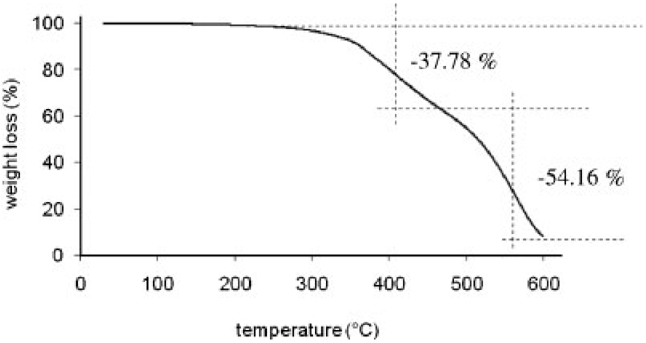
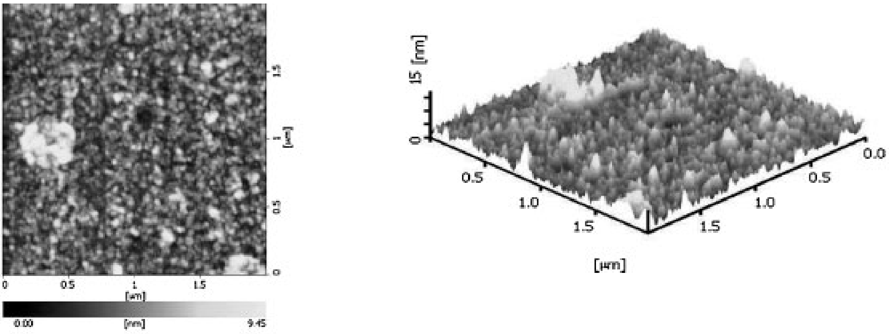
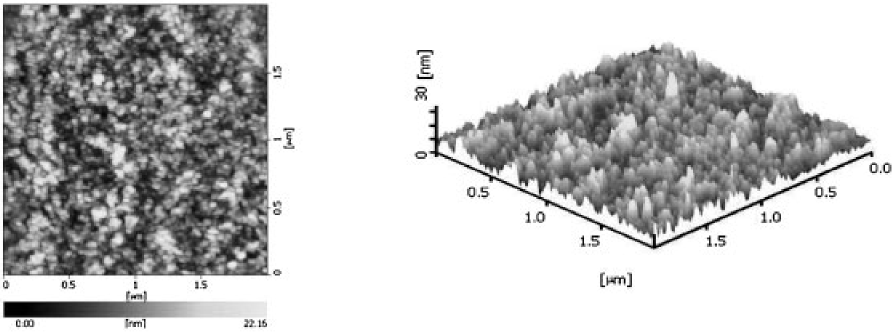


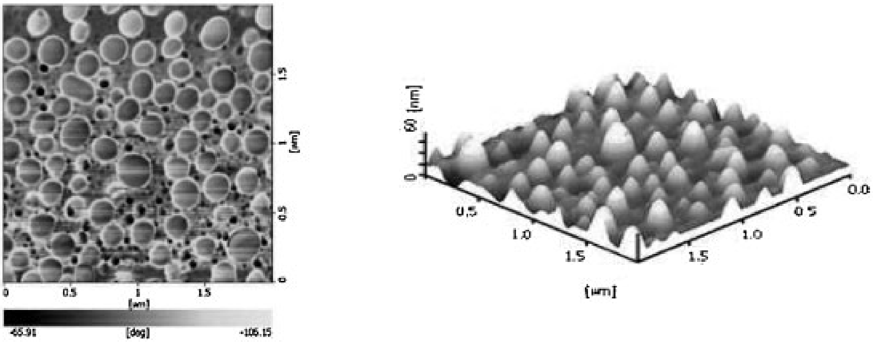
Figure 1.
TGA profile of the sample prepared from the precursor having the TIP:PDMS ratio of 1.0:1.5.



a) 60 °C, $R_a = 1.2$ nm



b) 100 °C, $R_a = 3.0$ nm



c) 200 °C, $R_a = 8.7$ nm

Figure 2.
AFM topographical images of the PDMS-based hybrid films coated on glass substrate heat-treated at 60–200 °C.

200 °C consisted of large protrusions of ~0.1–0.3 μ, and had higher surface roughness of 8.7 nm and lower contact angle of 91 degree. Based on the TGA result (Figure 1) which shows slight weight loss (few percents) at the temperature between 100–200 °C, it was believed that such large feature was formed as a result of evaporation and/or partial decomposition of organic constituents such as solvent or perhaps the PDMS molecules.

Values of contact angle and surface roughness of the films heated at various temperatures are summarized in Table 1. It has been reported that hydrophobicity depends on both surface topography and

Table 1.
Values of contact angle and surface roughness of the films obtained at difference heating temperature.

Heating temperature (°C)	Contact angle (degree)	Surface roughness (nm)
60	100 ± 0.2	1.2
100	99 ± 0.2	3.0
200	91 ± 0.3	8.7

chemical composition. High surface roughness usually gives rise to more hydrophobicity. Scale of roughness is also another important parameter to be taken into account. In this present study, it has been illustrated that fine protruding feature gave more hydrophobicity than larger, rounded feature although it has lower value of R_a.

Figure 3 shows the relationship between the value of contact angle and the TIP:PDMS ratio. Effect of heat-treated temperature on film's hydrophobicity is also illustrated. The precursor solutions used to prepare these films were aged for 2 days. At a given TIP:PDMS ratio, the contact angle decreased with increasing heat-treated temperature. The decrease of contact angle may be due to the effect of surface morphology as the surface changed from sharp to more rounded protrusion. The surface consisting large, round protrusion would have larger extend of contact area with water droplet and therefore exhibit lower contact angle. Partial decomposition of a low-energy PDMS to a higher-energy component was also another issue that could attribute to lower degree of hydrophobicity.

A maximum contact angle of 122° was obtained with TIP:PDMS molar ratio of 1.0:1.0, and heat-treated at 60 °C. The effect of TIP:PDMS ratio on film's hydrophobicity was inconclusive. It was expected that the hydrophobicity would increase with the increase of the PDMS content which was the constituent having low surface energy compared to the titanium hydrous oxide, provided that surface topography was unchanged at any TIP:PDMS ratio. However, this scenario might not be the case as surface topography might have changed. For instance, Iketani *et al.* reported that surface of the hybrid film became rougher and more porous with increasing PDMS content.[9]

Conclusions

Hydrophobic hybrid films of the PDMS and titanium (hydrous) oxide were successfully deposited on glass substrate by a sol-gel dip coating method. Surface hydrophobicity was found to be governed by topological feature (consisting of fine or rounded protrusions) created during post-heat treatment rather than degree of surface roughness. The effect of TIP:PDMS on film's hydrophobicity was inconclusive.

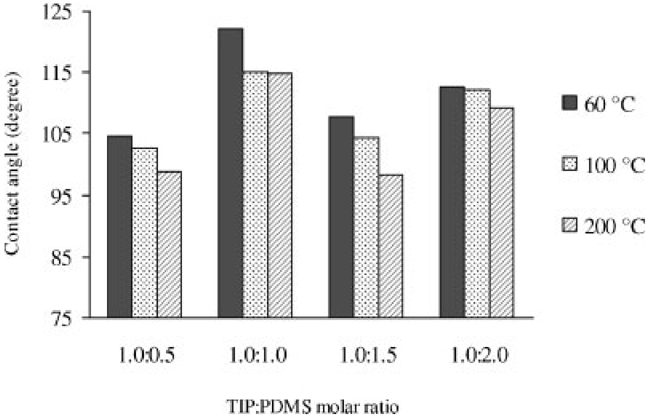


Figure 3.
Effect of TIP:PDMS molar ratio on surface hydrophobicity.

Acknowledgements: This research was supported by the National Metal and Materials Technology Center, the National Science and Technology Development Agency, Thailand (Grant MT-B-49-ATO-07-020-I).

[1] M. Ma, R. D. Hill, *Curr. Opin. Colloid Int. Sci.* **2006**, *11*, 193.
[2] L. Y. L. Wu, G. H. Tan, X. T. Zeng, *J. Sol-Gel. Technol.* **2006**, *38*, 85.
[3] T. Shindou, S. Katayama, N. Yamada, K. Kamiya, *J. Sol-Gel. Technol.* **2004**, *30*, 229.
[4] A. Nakajima, *J. Ceram. Soc. Jpn.* **2004**, *112*(10), 533.
[5] L. Y. L. Wu, A. M. Soutar, X. T. Zeng, *Surf. Coat. Tech.* **2005**, *198*, 420.
[6] N. Yamada, I. Yoshinaga, S. Katayama, *J. Sol-Gel. Technol.* **2000**, *17*, 123.
[7] R. Vogel, P. Meredith, I. Krtini, *Chem. Phys. Chem.* **2003**, *4*, 595.
[8] G. Camino, S. M. Lomakin, M. Lazzari, *Polymer.* **2001**, *42*, 2395.
[9] K. Iketani, R. D. Sun, M. Toki, K. Hirota, O. Yamaguchi, *J. Phys. Chem. Solid.* **2003**, *64*, 507.