

Surface Structure and Properties of (Oligourethane with Fluoroalkyl End Groups / Polyurethane) Blend Thin Films

Masafumi Horiuchi, Ken Kojio and Mutsuhisa Furukawa*

Graduate School of Science and Technology, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, JAPAN

Phone & Fax: +81-95-819-2651, e-mail: furukawa@net.nagasaki-u.ac.jp

Fluoroalkyl terminated oligourethane (FOU), which is synthesized with 1,4-butanediol (BD), 4,4'-diphenylmethane diisocyanate (MDI) and 2-(perfluorooctyl) ethanol (PFOE), was specially designed as a surface modifying additive. Surface structure and properties of the (FOU/polyurethane(PU)) blend thin films were investigated using X-ray photoelectron spectroscopy (XPS), static contact angle measurement and atomic force microscope (AFM). XPS and static contact angle measurement revealed that surface composition of the FOU molecules gradually increased with an increasing FOU content. This gradual increasing might be due to the strong interaction between hard segment unit, $-(\text{MDI-BD})_n-$, of the FOU molecules and PU matrix. The (FOU/PU) blend thin films exhibited the phase-separated structure, which is composed of the FOU domains and PU matrix. The number of the FOU domains increased with an increasing FOU content, corresponding to the results obtained from XPS and static contact angle.

Key Words: Surface Aggregation Structure, Polyurethane, Blend Film, Fluorinated Urethane Oligomer

1. Introduction

Surface structure and properties of materials are closely related to their functional properties, such as wettability, biocompatibility and so on.¹⁻⁸ Tremendous number of studies on the preparation of the polymer surface have done, for example, grafting reaction to the surface and polymer blend in order to obtain the functionalized material surfaces. However, these methods can not give the material surfaces which can satisfy our demands in terms of their properties and stability. Polyurethanes (PUs) are one of the most important polymers because they can show lots of properties only changing starting materials, reaction condition and content of hard and soft segments etc. PUs usually consist of the hard segment, which forms the strong hydrogen bond among them, and the flexible soft segment. The hydrogen bond energy for urethane groups is ca. 35.9 kJ mol⁻¹. This bond energy is fairly large and it can actually work as physical cross linking points, especially for the PU elastomers.

From these insights, our experiments began with the hypothesis that the hydrogen bonding between urethane repeating units might play a quite attractive role for the surface structure of the (oligourethane/polyurethane) blend thin films. We synthesized a surface modifying additive, which is the fluoroalkyl terminated oligourethane, and then,

prepared the blend thin films with base PUs. Hydrogen bonds between oligourethanes and matrix polyurethanes will give an intriguing influence for both formation and stabilization of surface structure, so that it solves the open question for the polymer surface.

In this study, we present the surface structure and properties of the (fluoroalkyl terminated oligourethane(FOU)/PU) blend thin films. We shall discuss about the effect of hydrogen bond as well as molecular weight and surface free energy of the FOU on the surface structure and properties of the blend thin films.

2. Experiment

2.1 Synthesis of polyurethane (PU)

The PU was prepared from poly(oxytetra-methylene) glycol (PTMG: $M_n=1944$, Mitsubishi Chemical Co., Ltd.), 4,4'-diphenylmethane diisocyanate (MDI, Nippon Polyurethane Industry, Co., Ltd.) and 1,4-butanediol (BD, Wako Chemical Co., Ltd.) by a prepolymer method. The PTMG was dried with bubbling dried nitrogen under a reduced pressure. Also, BD was refluxed with calcium chloride for 6 h, and then, distilled to remove involved water. MDI was used without any further purification.

The prepolymer was prepared from PTMG and MDI with the ratio of $K = [\text{NCO}]/[\text{OH}] = 3.3$ for 4 h

under a nitrogen atmosphere. The reaction was pursued by an amine equivalent method. After finishing the reaction, the prepolymer and curing agent were stirred well with the ratio of $[\text{NCO}]_{\text{pre}}/[\text{OH}] = 1.03$ for 30 s, and then, the viscous product was poured into the petri dish. The PU was postcured at 80 °C for 24 h in air.

2.2 Synthesis of FOU

The FOU was synthesized with MDI, BD and 2-(perfluorooctyl) ethanol (PFOE, Daikin Chemical Co., Ltd.) as an end-capping agent by a solution polymerization. Acetone was purified with general method to prevent the side reaction of isocyanate groups during reaction. Acetone solution of MDI was dropped into acetone solution of BD with the ratio of $K = [\text{NCO}]/[\text{OH}] = 1.4$ at 60 °C for 6 h and reacted for 3 h under a nitrogen atmosphere. Then, PFOE was added into the reaction solution to react with terminated isocyanate groups with the ratio of $[\text{NCO}]_{\text{pre}}/[\text{OH}] = 0.9$ for 3 h. In order to remove the residual PFOE after reaction, the product was dissolved into acetone and then it was filtered and dried at 80 °C. Chemical structure of the synthesized FOU was confirmed by elemental analysis, differential scanning calorimetry (DSC), Fourier-transform infrared (FT-IR) spectroscopy and proton nuclear magnetic resonance ($^1\text{H-NMR}$).

2.3 Preparation of the (FOU/PU) blend thin films

N,N-dimethylacetamide (DMA, Wako Chemical Co., Ltd.) solution of the PU was prepared with a concentration of 0.5 wt%. Then, the FOU was also dissolved into this solution with the blend ratio of 10/90, 15/85, 25/75, 35/65 and 50/50 (w/w) = (FOU/PU). The (FOU/PU) blend thin films were prepared from onto a silicon wafer by a dip coating method. Then, they were dried under a reduced pressure at 25 °C for 24 h.

2.4 X-ray photoelectron spectroscopy (XPS)

The surface chemical composition of the (FOU/PU) blend thin films was evaluated using XPS. The XPS spectra were obtained with an ESCA-850 (Shimadzu Co., Ltd.) at room temperature. The XPS measurement was performed under a conventional condition with an $\text{MgK}\alpha$ source at 8 kV and 30 mA. The emission angle of the photoelectron was adjusted to 15°, 30° and 90°. The main chamber of the XPS instrument was maintained at $\sim 10^{-6}$ Pa. The peak

position of neutral carbon in $\text{C}_{1\text{S}}$ spectra was calibrated to 285.0 eV in order to remove the charging energy shift.

2.5 Static contact angle measurement

Water contact angle of the (FOU/PU) blend thin films was measured with a DROPMASTER 300 (Kyowakaimen-kagaku Co., Ltd.). Measurements were carried out with ca. 1.0 μL purified water droplet. To avoid the uncertainty of the measurement, the average of 15 measurements were taken from each sample.

2.6 Atomic force microscope (AFM)

The surface morphology of the (FOU/PU) blend thin films was observed using an AFM with the intermittent mode. The AFM images were obtained by an SPA 400 with an SPI 3800 controller (Seiko Instruments Industry Co., Ltd.) at room temperature in air. The AFM cantilever used (SI-DF20, Seiko Instruments Industry Co., Ltd.) was microfabricated from Si, and its spring constant was 14 N m^{-1} .

3. Results and Discussion

The surface chemical composition of the (FOU/PU) blend thin films was analyzed by XPS. Figure 1 shows the $\text{F}_{1\text{S}}$ and $\text{C}_{1\text{S}}$ spectra of the PU and (FOU/PU) blend thin films with various FOU content at the emission angle of 90°. The peak assigned to the fluorine atom was clearly observed at 690.0 eV for all (FOU/PU) blend thin films, but not for the PU thin film. On the contrary, four peaks were detected for the $\text{C}_{1\text{S}}$ spectra of the (FOU/PU) blend thin films. The peaks observed at 285.0, 286.5, 289.5 and 292.0 eV can be assigned to the neutral (-C-C*-C-), ether

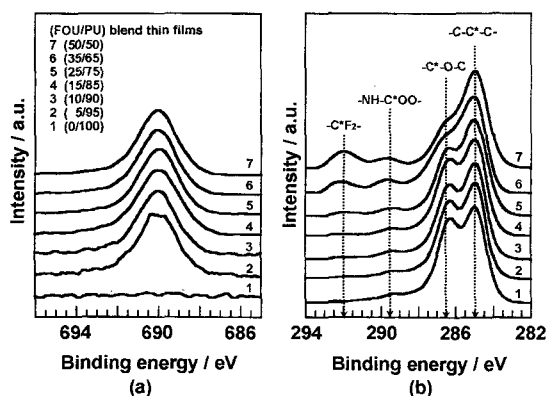


Figure 1. XPS (a) $\text{F}_{1\text{S}}$ and (b) $\text{C}_{1\text{S}}$ spectra for the (FOU/PU) blend thin films with various blend ratios at the emission angle of 90°.

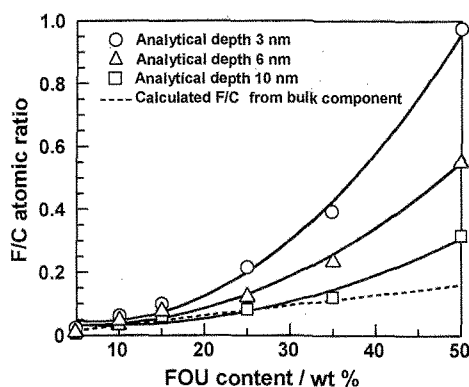


Figure 2. FOU content dependence of surface F/C atomic ratio for (FOU/PU) blend films. Dotted line denotes F/C value calculated from bulk component.

(-C*-O-C-), urethane carbonyl (-NH-C*OO-) and fluoromethylene (-C*F₂-) carbons, respectively. As the FOU content increases, -C*F₂- and -C*-O-C- peaks increased and decreased, respectively. Since these two -C*F₂- and -C*-O-C- peaks are from FOU and PTMG, respectively, this result clearly indicates that the FOU molecules segregate at the blend thin film surface with increasing FOU content.

Figure 2 shows the FOU content dependence of surface F/C atomic ratio for the (FOU/PU) blend thin films determined from Figure 1. The magnitude of F/C was calculated from peak area of fluorine (F_{1s}) and carbon (C_{1s}). F/C for the bulk was also shown in Figure 2. For the FOU content up to 15 wt% blend thin films, F/C value was comparable with that for bulk. In contrast, for the blend thin films with the FOU content of 15 - 50 wt%, F/C remarkably became larger than for bulk with an increasing FOU content. Furthermore, for the data at analytical depth 3 nm, F/C strongly depends on the FOU content. These results obviously imply that fluoroalkyl chains segregated at the top of blend films surface. Generally, it is well-known that fluoroalkyl chains segregate at the material surface due to its low surface free energy even if its content is quite low. Thus, F/C tends to show a constant large value for the FOU content even at the low FOU content because of segregation of fluoroalkyl chains at the surface.⁴ However, F/C gradually increased with an increasing FOU content in this study. This may be due to the strong interaction between crystalline -(MDI-BD)_n- units of the FOU molecules and the hard segment chains in the PU matrix. It was revealed that the -(MDI-BD)_n- units can easily crystallize and form the hydrogen bond between them.¹⁰ That is, this strong interaction between

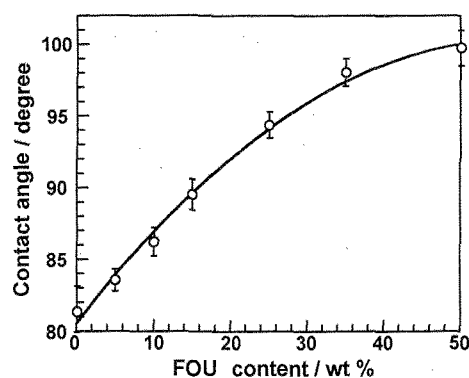


Figure 3. FOU content dependence of water contact angles for (FOU/PU) blend thin films. Error bar indicates standard deviations.

-(MDI-BD)_n- units of the FOU and PU prevents the segregation of the FOU at the top surface. The discussion relating this phenomena will be given later with morphological observation with AFM.

Figure 3 shows the static water contact angles for the (FOU/PU) blend thin films with various FOU contents. Contact angles increased with an increasing FOU content. These results indicate that the fluoroalkyl chains were segregated at the surface with an increase of FOU content. For the material surface covered with fluoromethyl groups, static water contact angle exhibits much larger magnitude (> 110°).⁹ Thus, it seems that the FOU molecules were not able to completely cover the top surface with fluoroalkyl end groups even at high FOU content (50 wt%) since the water contact angle of the (FOU/PU) blend thin film far below 110°.

The FOU content dependence of water contact angle and F/C by XPS showed similar trend, however, there is an important difference. The F/C obtained by XPS increased monotonically with increasing FOU content, in contrast, water contact angle was almost saturated above 35 and 50 wt% of the FOU content. This trend might be able to be explained taking into consideration of the molecular orientation of the FOU molecules. To understand the reason, we performed AFM observation for these blend thin films.

Figure 4 shows the AFM images of the (a) PU and (b) (FOU/PU) (10/90) blend thin film. Both AFM images exhibited uneven surface. This would be the characteristic of the PU films. For the (FOU/PU) (10/90) blend thin film (Figure 4(b)), a number of small dots, as well as uneven surface observed for the PU film, were observed. Diameter of these domains was ca. 70 nm.

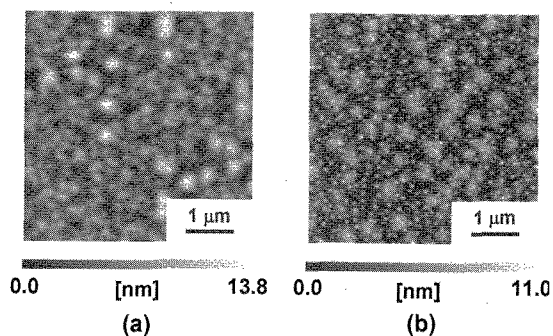


Figure 4. AFM images of (a) PU thin film and (b) (FOU/PU) (10/90) blend thin films. Scanning area is $5 \times 5 \mu\text{m}^2$.

Figure 5 shows the AFM images of the (FOU/PU) blend thin films with FOU content 15 – 50 wt%. For the (FOU/PU) (15/85) blend thin film (Figure 5 (a)), domains was larger in comparison with the (FOU/PU) (10/90) one (diameter: 70 nm), indicating that the island domains were composed of the FOU component. Furthermore, with an increase in the FOU content, the FOU domains were connected together as shown in Figure 5 (b) and (c). For the (FOU/PU) (50/50) blend thin film (Figure 5(d)), isolated domains were formed again. This result can be explained as follows with the combination of static contact angle and XPS, AFM. The FOU molecules formed the domains without any orientation at a surface FOU content below 35 wt% because many of the FOU molecules can have an interaction with the hard segment units of the PU with a formation of hydrogen bonding between urethane

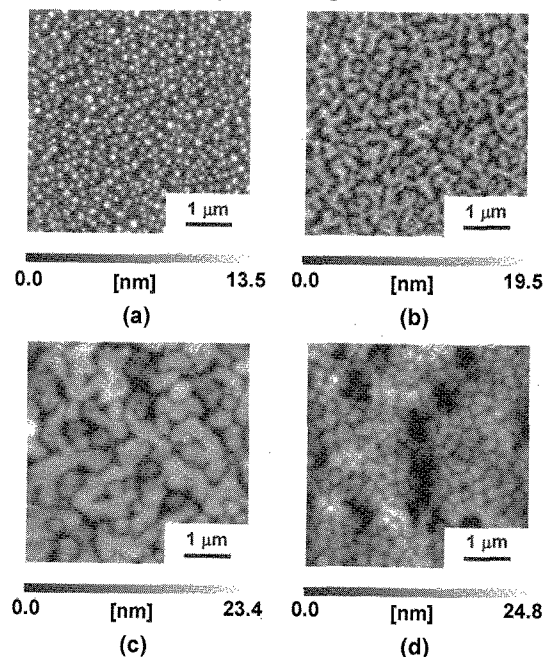


Figure 5. AFM images of (a) (FOU/PU) (15/85), (b) (25/75), (c) (35/65), (d) (50/50) blend thin films. Scanning area is $5 \times 5 \mu\text{m}^2$.

groups (The FOU molecules are trapped into the PU matrix.). On the other hand, for the (FOU/PU) (50/50) blend thin film, since the FOU molecules without interaction with the PU hard segment units would increase, fluoroalkyl chains of the FOU seem to orient easily normal to the surface. It seems that this deduction can only explain well the difference in the FOU content dependence of F/C and water contact angle and the change in morphology with FOU content.

4. Conclusions

The (FOU/PU) blend thin films were prepared onto a silicon wafer, and surface structure and properties were investigated. Surface composition of the FOU component and water contact angle increased with an increasing FOU content. Surface structure of the (FOU/PU) blend thin films showed the phase-separated structure, which is composed of the FOU domains and PU matrix. Phase-separated structure and the degree of the segregation of the FOU molecules at the blend film surface were changed with the FOU content on account of the effect of the interaction between urethane groups of the FOU and PU matrix, as well as the surface free energy and molecular weight of the FOU molecules.

5. References

- [1] D. Wang, J. Ji and L. X. Feng, *Macromolecules*, **33**, 8472-8478 (2000).
- [2] Y. S. Kim, J. S. Lee, Q. Ji, and J. McGrath, *Polymer*, **43**, 7161-7170 (2002).
- [3] W. Ming, M. Tian, R. D. van de Grampel, F. Melis, X. Jia, J. Loos and R. van der Linde, *Macromolecules*, **35**, 6920-6929 (2002).
- [4] C. B. McCloskey, C. M. Yip and J. P. Santerre, *Macromolecules*, **35**, 924-933 (2002).
- [5] M. J. Dalby, M. O. Riehle, H. Johnstone, S. Affrossman and A. S. G. Curtis, *Biomaterials*, **23**, 2945-2954 (2002).
- [6] Y. W. Tang, J. P. Santerre, R. S. Labow, and D. G. Taylor, *J. Appl. Polym. Sci.*, **62** 1131-1145 (1996).
- [7] R. Jahangir, C. B. McCloskey, W. G. Mc Clung, R. S. Labow, J. L. Brash, J. P. Santerre, *Biomaterials*, **24**, 121-130 (2004).
- [8] Y. W. Tang, J. P. Santerre, R. S. Labow and D. G. Taylor, *J. Biomed. Mater. Res.*, **35**, 371-381 (1997).
- [9] K. Kojio, A. Takahara and T. Kajiyama, *ACS Symp. Ser.*, **787**, 31-45 (2001).
- [10] J. Backwell, C. D. Lee, *J. Polym. Sci. Polym. Phys.*, **22**, 759-779 (1984).