1.2 Microphase Separated Structure and Surface Properties of Fluorinated Polyurethane Resin

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ABSTRACT

The effect of fluorination on microphase separation and surface properties of segmented polyurethane (PU) resin were investigated. A series of fluorinated polyurethane resin (FPU) was synthesized by reacting a fluorinated diol with aromatic diisocyanate. The microphase separated structure of FPU was studied by thermal analysis, and small angle X-ray scattering (SAXS) as well as wide angle X-ray diffraction (WAXD). The surface structure and properties were characterized by X-ray photoelectron spectroscopy (XPS) and dynamic contact angle measurement. The incorporation of fluorine into hard segment brings the FPU to have a higher hard domain cohesion and increase the phase separation, however localization of fluorine on the surface could not be observed. On the other hands, localization of fluorine on the surface could be achieved for soft segment fluorinated PU without any significant change in microphase separated structure. The results from this study give an important basic information for designing PU coating material with a low surface energy and strong adhesion as well as for development of release film on pressure sensitive adhesive tape.

INTRODUCTION

Linear or segmented polyurethanes resin (PU), are multi block copolymers, consisting of hard and soft segments. It is well known that incompatibility between both segments leads PU to have a microphase separated structure[1]. This peculiar structure brings PU to be used in various ways such as, elastomers, adhesives, artificial organ, and coating. Regarding to these kinds of applications, it is necessary to characterize and control their surface and interfacial properties. Therefore, relationships between the microphase separated structure and the surface properties of this material is of important to be clarified[2,3].

In other hands, fluorination of PU may lead this material to have a unique balance properties such as low surface energy, low coefficient of friction,and high solvent and chemical resistance. Fluorinated polyurethane (FPU) are widely used in modern chemical technology. They are used in products ranging hard, heat-resistant electrical component to biologically compatible surgical adhesive. Perhaps the largest use of FPU is in surface coating for industrial and residential structure, automobile, ships and aircraft. FPU are also used widely in medical product and as surface-enhancing treatments of textiles, leather and carpets. The information about FPU is abundant in patent but it is found relatively little in journal and books. Some studies have been done on hard segment fluorinated PU [4-7], and

some others on soft segment fluorinated PU [9,10] but the relationship between microphase separation phenomena and surface properties of FPU is not yet clear.

In this study, we investigated the effect of incorporation of fluorine onto both microphase separated structure and surface properties as well as their relationship.

EXPERIMENTAL

Materials

A series of FPU based on methylene diphenylene diisocyanate (MDI) and butanediol (BD) as hard segment (HS) and polypropylene glycol (PPG, Mn=1000) as soft segment (SS) was synthesized. Hard segment fluorinated PU (H-FPU) were prepared by replacing a part of BD with 2,2,3,3-tetrafluoro 1,4-butanediol (TFBD). While the soft segment fluorinated PU (S-FPU) were prepared by using perfluoropolyether knowing as fomblin® ZDOL (Mn=1000) instead of PPG. The reaction procedure and the chemical structure are shown in fig.1. Detailed explanation of the sample preparations were reported elsewhere[2].

Characterizations

The microphase separated structure of FPU cast film was studied by differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS).

The DSC measurements were done by Seiko Instruments DSC 220 CU. The WAXD profile was obtained by symmetrical reflection geometry with Cu Kα radiation generated at 40 kV, 20 mA. The SAXS profiles were obtained using nickel-filtered Cu Kα irradiation generated at 40 kV, 200 mA by a Mac Science diffraction unit equipped with Kratky camera.

The surface structure was characterized by X-ray photoelectron spectroscopy (XPS), a Shimadzu ESCA-850 with MgKα X-ray source operated at 8 kV, 20 mA. The surface properties was analyzed by a dynamic contact angle measurement[2].

RESULTS AND DISCUSSION

Effect of incorporation of fluorine into the HS on the crystallinity of PU was investigated by WAXD as shown in figure 2. The figure shows the WAXD profiles of FPU having various TFBD contents. The higher TFBD content, the crystalline diffraction peaks was more obvious. These results corresponded to an increase of the crystallinity[11]. The change in crystallinity was also observed by DSC measurement in which all samples exhibited melting endhoterms, but the melting peaks shifted to a higher temperature with the increase of TFBD content. Both results suggest that the fluorination of HS increased the crystallinity of PU. In other word, the incorporation of fluorine into the HS seems to improve the cohesion of hard domain.

Figure 3 shows the SAXS profiles of the H-FPU with various TFBD content. All samples show an appearance of peek at about same q value, which are considerable as interdomain distance, c.a 25 nm. The peak intensity, however, increase and become sharper with the TFBD contents. It shows that the contrast between hard and soft domain increased with fluorine content in HS[10,11]. It means the separation between hard and soft domain increase with the increasing of fluorine contents in the HS. In other word, the H-FPU does possess more phase separated structure than the control.

Figure 4 shows the relationship between the TFBD content and fluorine atomic percent on the surface of H-FPU from XPS measurement. Dotted line represents the

calculated value based on the averaged composition. Percentage of observed fluorine increase with TFBD content, but the value are lower than the calculated one. It means fluorine-rice surface could not be obtained by incorporating fluorine into HS. It may be due to an increase in microphase separated structure in the bulk as discussed before. An increase in microphase separation may decrease the HS mobility needed for migration to surface, and lead the SS to more dominate the surface.

From above result and discussion, it is clear that incorporation of fluorine into the HS of segmented polyurethane affected the microphase separated structure as well as surface properties. It is also clear that microphase separation in the bulk of PU affects the surface structure.

Figure 5 shows the wide angle X-ray diffraction profiles of S-FPU having various ZDOL contents. There is no significant change in profile characteristic with the increasing fluorine contain in SS. This result suggest that the fluorination of SS did not change the crystallinity of PU. No significant change in crystallinity was also observed by DSC measurement in which all samples exhibited melting endhoterms, and the melting peaks almost same at around 190 °C.

Figure 6 shows the SAXS profiles of the S-FPU with various ZDOL content. All samples show an appearance of peek at about same q value, means that interdomain distance did not change with fluorine content in SS. In contrast with H-FPU however, the peak intensity decrease with the ZDOL contents. The incorporation of fluorine into SS increase the electron density of soft domain, so that reduce the contrast between hard and soft domain. The HS packing in hard domain however, was not change with ZDOL content as determined by WAXD and DSC.

Figure 7 shows the relationship between the ZDOL content and atomic percent of fluorine on the surface and the interface of S-FPU. The interface was measured soon after peeling off the sample from aluminum (Al) substrate. Percentage of fluorine on the surface significantly higher than the interface at entire range of ZDOL contents. It means that fluorine were localized on the surface more than on the interface.

Figure 8 shows the relationship between the ZDOL content and water contact angle on the surface of S-FPU. The averaged values of contact angle increased up to 90 degree by incorporating 0.5 mol. % of ZDOL and then seem to be constant at this high contact angle with the increasing of ZDOL content. This result is as expected for preparing polymer with low surface energy by fluorination.

The unsymmetrical structure between surface and interface, fluorine-rich and fluorine-poor, respectively, may be desired to provide a PU coating material with a low surface energy and strong adhesion. It is also desired for development of release film on pressure sensitive adhesive tape.

CONCLUSION

Fluorination of hard or soft segment of PU affected both microphase separation and surface properties. In other word, the microphase separated structure and surface properties of FPU can be controlled by incorporating fluorine. Incorporation of fluorine into HS brings the PU to have a higher hard domain cohesion, but localization of fluorine on the surface could not be observed. On the other hands, the localization of fluorine on the surface could be observed for soft segment fluorinated PU without any significant change in microphase separated structure. Thus, it is also clear that the microphase separated structure

and surface properties of PU can be controlled by changing the fluorine content as well as the fluorination place.

The results from this study give an important basic information for designing PU coating material with a low surface energy and strong adhesion as well as for development of release film on pressure sensitive adhesive tape.

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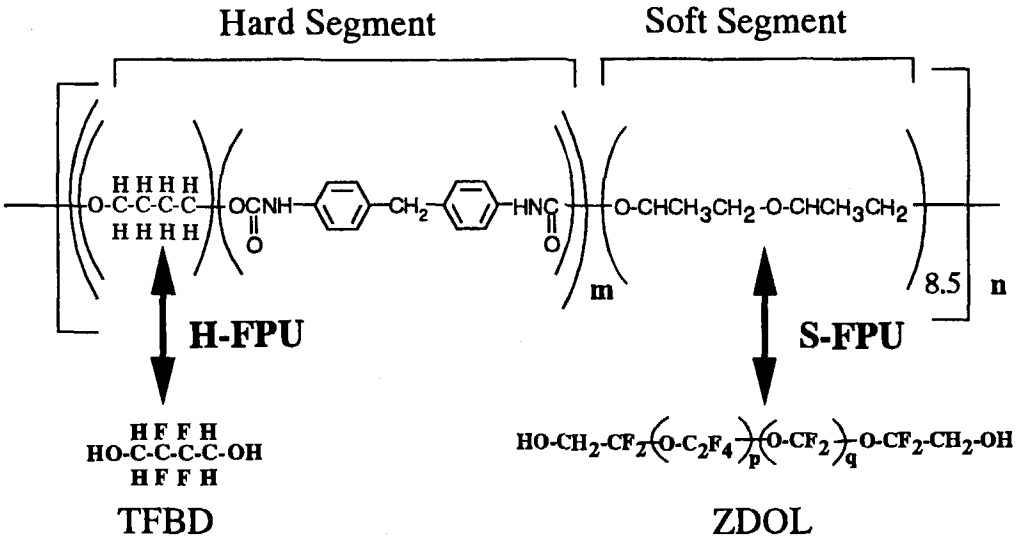

Figure 1 Chemical formula of segmented polyurethane and materials used for fluorination.

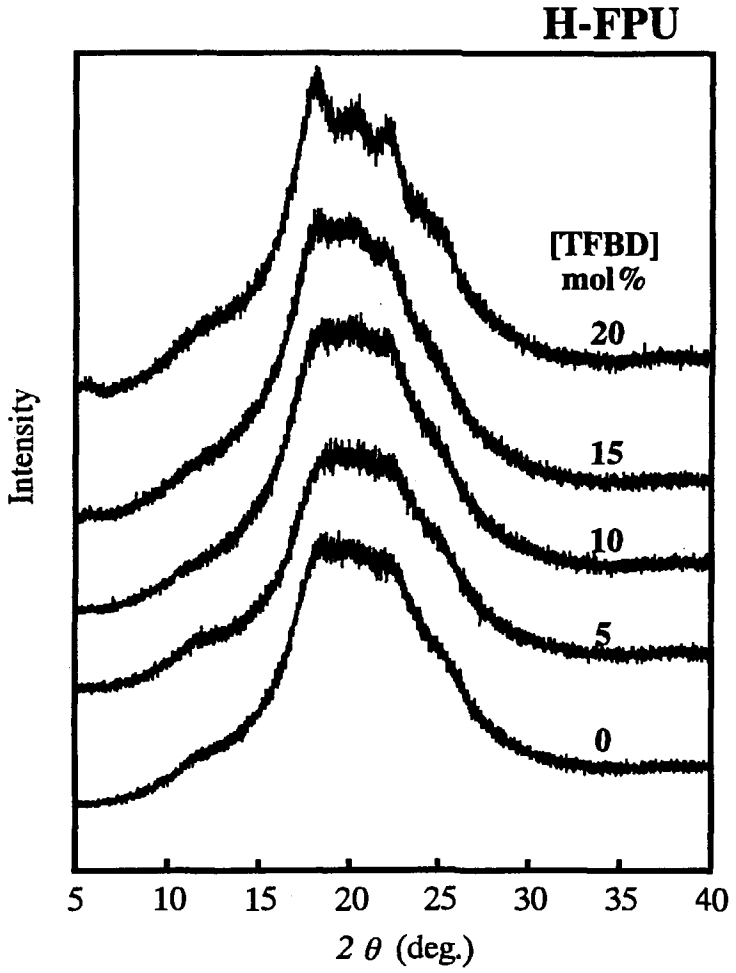

Figure 2 X-ray diffraction profiles of the H-FPU with various TFBD contents.

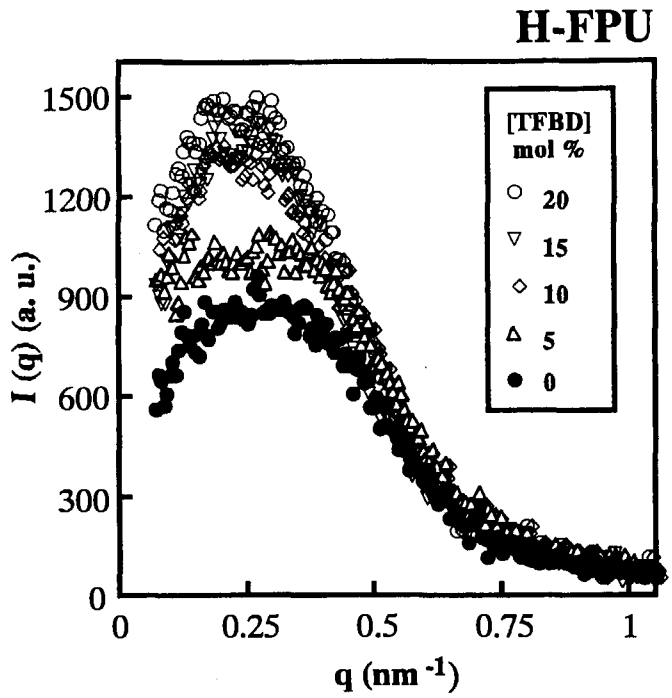

Figure 3 SAXS profiles of the H-FPU with various TFBD contents.

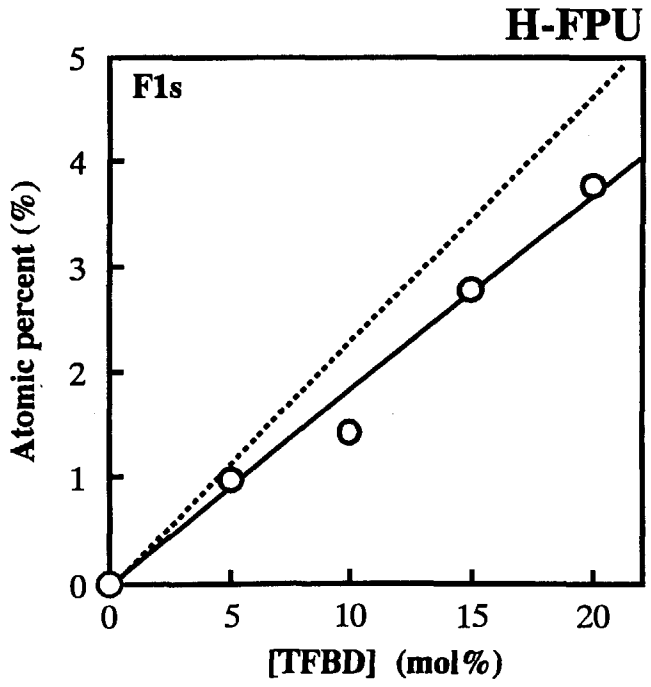

Figure 4 Relationship between the TFBD content and the atomic percentage of fluorine on the surface of H-FPU from XPS measurement. Dotted line represents the calculated value based on the averaged composition.

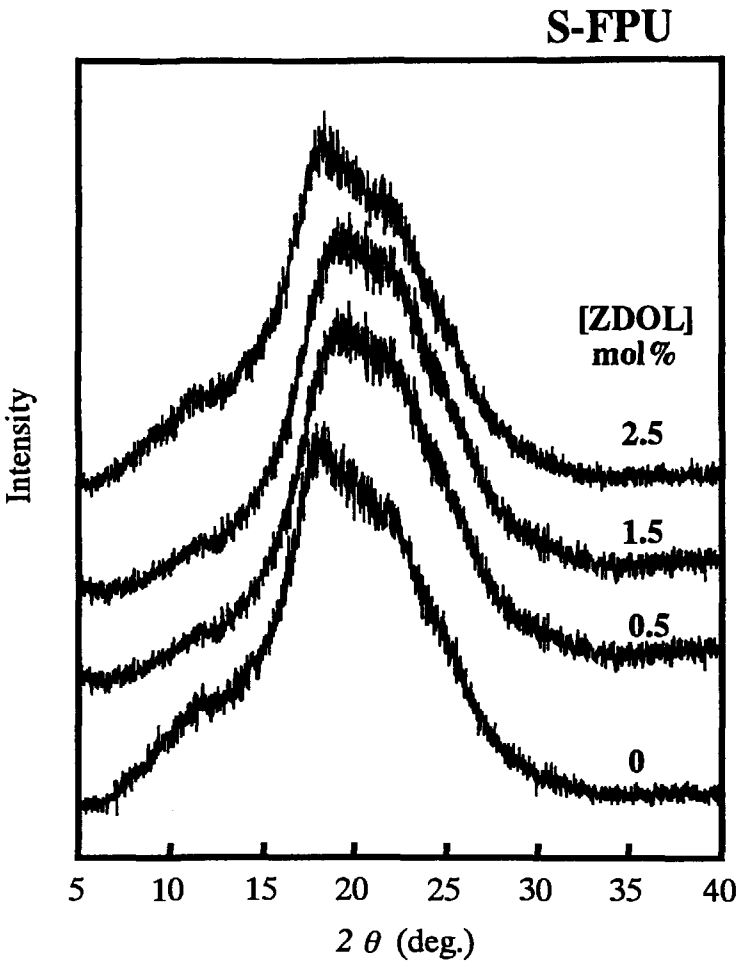

Figure 5 X-ray diffraction profiles of the S-FPU with various ZDOL contents.

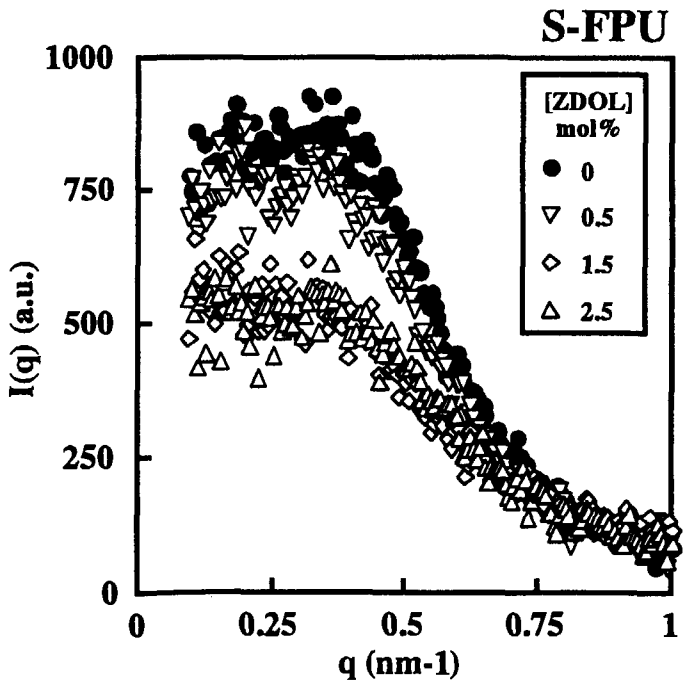

Figure 6 SAXS profiles of the S-FPU with various ZDOL contents.

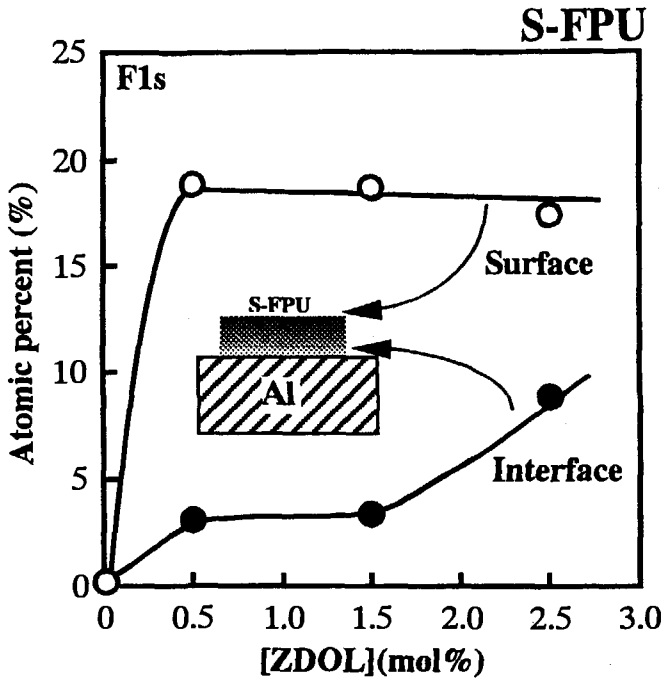

Figure 7 Relationship between the ZDOL content and the percentage of Fluorine localized on (○) surface and (●) Aluminum interface of FPU from ESCA measurement.

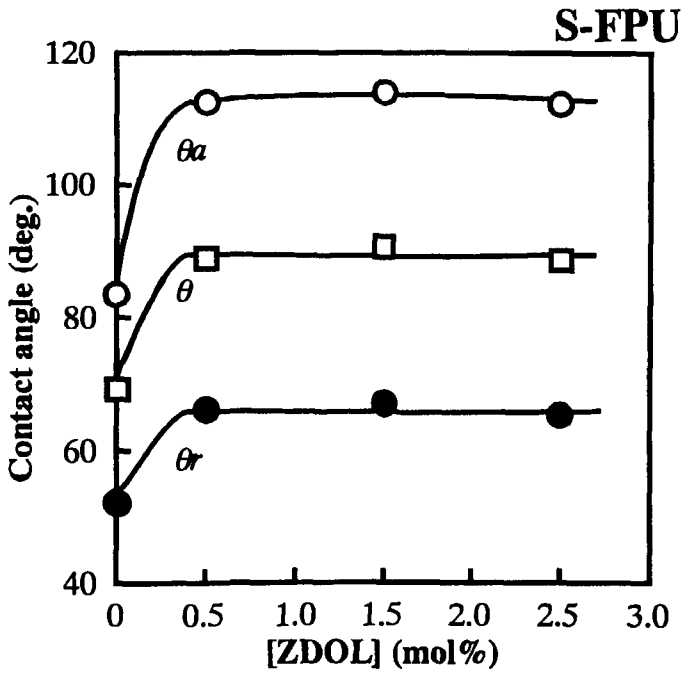

Figure 8 Relationship between the ZDOL contents and the contact angle of water on S-FPU.