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State of Aggregation and Surface Chemical Composition of Composite Thin Films Composed of Poly(vinyl alcohol) and Fluorocarbon Amphiphile

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ABSTRACT: Structural characterization of composite thin films composed of poly(vinyl alcohol) and a fluorocarbon amphiphile has been carried out. The wide-angle X-ray diffraction study revealed that the fluorocarbon amphiphile in the composite thin film forms bimolecular lamellae. The bimolecular lamellae were oriented parallel to the surface of the composite thin films. X-ray photoelectron spectroscopy showed enrichment of fluorocarbon groups on the surface of the composite thin film owing to the lower surface free energy of fluorocarbon groups compared with that of PVA. The surface of the composite film is completely covered with fluorocarbon amphiphilic molecules even when the weight fraction of fluorocarbon amphiphile is very small.

Introduction

Organic compounds containing fluorocarbon components show unique properties due to the low surface free energy of CF_2 and CF_3 groups. Some fluorocarbons have been used as artificial blood since they dissolve molecular oxygen very well.[1,2] One of the authors succeeded in preparing an oxygen enrichment membrane composed of polymer, liquid crystal, and fluorocarbon monomers.[3,4] One of the most important industrial application of organic compounds containing fluorine is the surface treatment of textiles and plastics by utilizing the surface-active effect of fluorocarbon groups.[5] As adhesion between a fluorocarbon surface and other compounds is very weak, such surfaces show nonadhesive properties. Therefore, the characteristic property for preventing contamination of surfaces is obtained by adding a small amount of surfactant containing fluorocarbon groups.[3]

A series of amphiphiles containing fluorocarbon have been synthesized by Kunitake and co-workers.[6,7] Fluorocarbon amphiphiles form a bilayer structure in water and exhibit phase transition behavior similar to that observed for biological lipids or other artificial hydrocarbon amphiphiles.[8-10] The fluorocarbon amphiphiles can be immobilized by casting a water solution of amphiphile with aqueous poly(vinyl alcohol). A gas permeation experiment through this immobilized film revealed that the permeation rate of oxygen was 2.4–2.7 times as fast as that of nitrogen.[11] This oxygen-enriching property was observed even when the weight content of fluorocarbon amphiphile was less than 10%.

In this paper, the surface chemical composition of the composite thin film composed of poly(vinyl alcohol) and fluorocarbon amphiphile has been studied by X-ray photoelectron spectroscopy. Also, the state of aggregation of the components was investigated on the basis of X-ray diffraction studies and morphological observation.

Experimental Section

1. Sample Preparation. The fluorocarbon amphiphile and polymer used in this study are shown in Figure 1. The amphiphile containing fluorine was prepared by the standard procedure.[6,7] The fluorocarbon amphiphile forms a stable bilayer membrane in water. The fluorocarbon amphiphile was dispersed in water by sonication and the dispersion was mixed with a water solution of poly(vinyl alcohol) (PVA) (MW = 154 000). The composite thin film was prepared by casting a water solution of PVA with the fluorocarbon amphiphile on a clean glass plate at room temperature; the cast film was then extensively dried in vacuo. The weight fraction of the fluorocarbon amphiphile in the composite thin film was varied from 19 to 83 wt %.

2. Measurements. In order to characterize the state of aggregation of PVA and the fluorocarbon amphiphile in the composite thin films, scanning electron micrograph (SEM) observation and X-ray diffraction study were carried out. The morphological observation of the composite thin film was carried out by using

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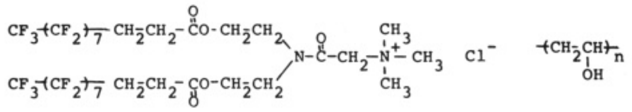

$2C^F_8C_3$-de C_2N^+ PVA

Figure 1. Chemical structures of fluorocarbon amphiphile and poly(vinyl alcohol) (PVA).

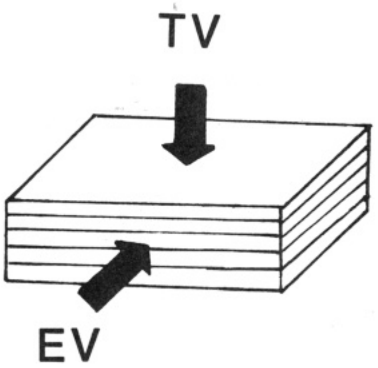

Figure 2. Direction of incident X-ray beam. Directions normal and parallel to the film surface are designated as through view (TV) and edge view (EV).

scanning electron microscope (SEM). The composite thin film was fractured in liquid nitrogen and the fracture surface was observed with SEM (S-430, Hitachi Co., Ltd).

Wide-angle X-ray diffraction (WAXD) patterns of the composite thin films were obtained by using a toroidal focusing camera attached to a Rigaku X-ray generator RU-200. All X-ray beams were generated with Cu Kα radiation filtered by nickel foil. The X-ray diffraction photographs of a multilayered thin film of about 1 mm in thickness were taken with the X-ray beam normal (through view, TV) and parallel (edge view, EV) to the film surface, as shown in Figure 2.

The surface composition of the composite thin film was investigated by X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained on an ESCA 750 photoelectron spectrometer (Shimadzu Co., Ltd.) using Mg Kα which was operated at 8 kV and 30 mA. The samples on the probe were cooled to 240 K to avoid degradation and evaporation of amphiphiles during measurements. Spectra were obtained in digital form. Curve fitting of the spectra was accomplished by using a nonlinear least-squares method.[12] A Gaussian–Lorentzian product function was used to resolve the C_{1s} peak into its components. The charging shift was referenced to the C_{1s} line emitted from neutral hydrocarbon (285.0 eV).

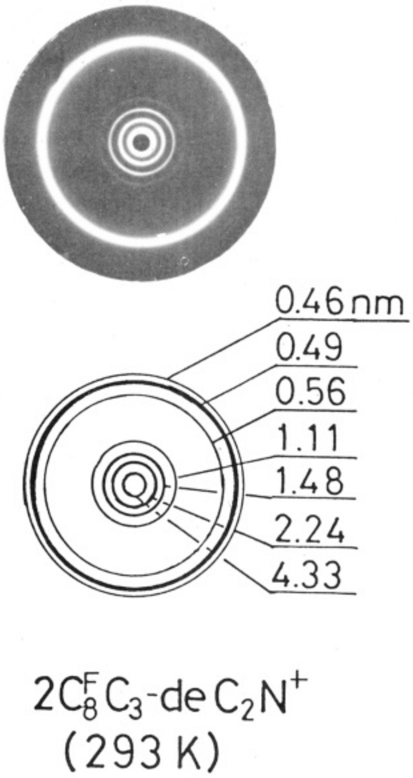

Figure 3. Wide-angle X-ray diffraction pattern of fluorocarbon amphiphile (powder) at 300 K.

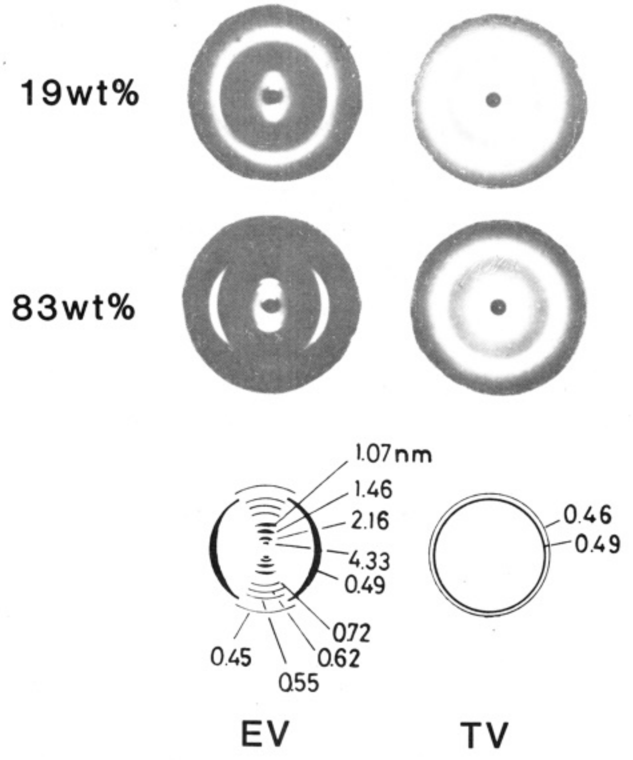

Figure 4. Wide-angle TV and EV diffraction patterns for composite thin films containing fluorocarbon amphiphile of 19 and 83 wt %.

Results and Discussion

1. Aggregation State of Composite Thin Films. The aggregation state of amphiphile molecules in the composite thin film was studied by wide-angle X-ray diffraction. Figure 3 shows the wide-angle X-ray diffraction pattern of the powder of fluorocarbon amphiphile at room temperature. Since the phase transition temperature of fluorocarbon amphiphile is 351 K,[11] this amphiphile is in a crystalline state at room temperature. The fluorocarbon amphiphile shows X-ray reflections corresponding to 4.33-, 2.24-, 1.48-, and 1.11-nm spacings. As the reciprocal spacings from the fluorocarbon amphiphile are in the ratio of 1:1/2:1/3:1/4, this fluorocarbon amphiphile aggregates in a bimolecular lamellar form.[13] The wide-angle X-ray reflections of 0.46, 0.49, and 0.56 nm were observed in the case of a crystalline state of fluorocarbon amphiphile. These reflections became a halo above the crystal-liquid crystal phase transition temperature, T_c. This indicates that these reflections are related to the melting of fluoroalkyl chains in the fluorocarbon bilayer lamella. Figure 4 is the WAXD patterns for the composite thin films containing the fluorocarbon amphiphile of 19 and 83 wt %. When the X-ray beam was irradiated perpendicular to the film surface (TV), two Debye rings corresponding to intermolecular spacings of 0.46 and 0.49 nm were observed. However, the TV diffraction pattern did not show any reflection related to the lamellar structure. When the X-ray beam was irradiated parallel to the film surface (EV), the WAXD patterns showed the orientation of bi-

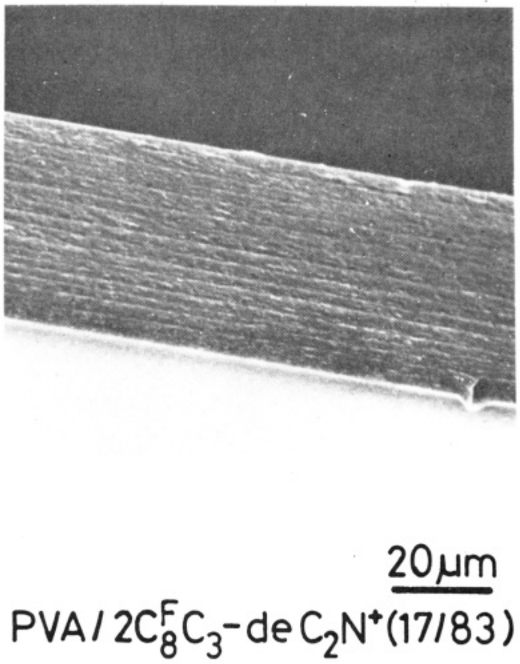

Figure 5. Scanning electron micrograph of the fracture surface of composite thin film containing fluorocarbon amphiphile of 83 wt %.

molecular lamella perpendicular to the film surface. On the meridian of EV, the higher order reflections attributed to the bilayer lamellar structure were observed. This result indicates that the fluorocarbon amphiphile forms bilayer lamellae parallel to the surface of the composite thin film. The intensity of these reflections became more distinct with an increase in the weight fraction of fluorocarbon amphiphile. The absence of these small-angle reflections on TV supports that the orientation of the bilayer lamellae is almost parallel to the film surface.

The composite thin film was fractured in liquid nitrogen in order to observe its inner morphology with a scanning electron microscope. Since liquid nitrogen temperature is much lower than the glass transition temperature of PVA and the phase transition temperature of the fluorocarbon amphiphile, the fracture surface clearly exhibits its internal structure without artifacts. Figure 5 shows the scanning electron micrograph of the composite thin film containing 83 wt % fluorocarbon amphiphile. Although PVA homopolymer showed the smooth surface characteristic of brittle failure, distinct striations parallel to the film surface were observed inside the composite thin film. As the X-ray diffraction study revealed the orientation of bimolecular lamellae perpendicular to the film surface, these striations may be related to the aggregation of the bimolecular lamellae of amphiphile molecules in the composite thin film. These striations became less distinct with a decrease in the weight fraction of the fluorocarbon amphiphile. Polarized optical microscopic observation was carried out to investigate the orientation of the amphiphile molecules in the composite thin film. The incident light was perpendicular to the surface of the composite thin films. The PVA film and the composite thin film used in this study showed a dark field under crossed nicols. This indicates that the orientation of the amphiphile molecular axes is nearly perpendicular to the film surface. This result is consistent with the X-ray diffraction results as shown in Figure 4.

2. Surface Chemical Composition of Composite Thin Film. The surface chemical composition of the composite thin films was analyzed by X-ray photoelectron spectroscopy (XPS). Figure 6 shows the geometry of the XPS measurement. The angle between the sample surface and the direction of analyzer is called the takeoff angle. The sampling depth, d, can be represented by the following equation:

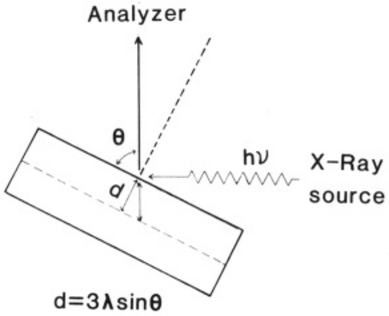

Figure 6. Relationship between the incident X-ray beam and emitted photoelectron at a takeoff angle of θ.

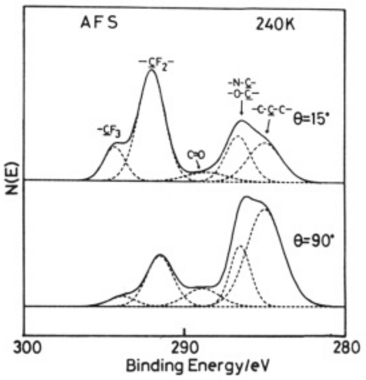

Figure 7. X-ray photoelectron spectra for the air facing surface (AFS) of a composite thin film containing fluorocarbon amphiphile of 19 wt % at the takeoff angles of 15° and 90°.

$$d = 3\lambda \sin \theta \tag{1}$$

where θ and λ are takeoff angle of photoelectron and photoelectron mean free path in the specimen, respectively. The sampling depth is defined as the depth from which 95% of the signal is detected.[14] Therefore, the relative signal intensity from the outermost surface increases with a decrease in the takeoff angle.

Figure 7 shows the XPS spectra of C_{1s} for the air facing surface (AFS) of the composite thin film containing fluorocarbon amphiphile of 19 wt % at the takeoff angles of 90° and 15°. The XPS measurement was carried out under the specimen temperature of 240 K at which degradation of amphiphile was decisively reduced. This is confirmed by the variation of XPS intensity with the X-ray irradiation time. At room temperature, the intensity of F_{1s} decreased with an increase in the X-ray irradiation time due to the dissociation of the C–F bond. However, the intensity of F_{1s} did not change at the measurement temperature of 240 K. The C_{1s} peak corresponding to the aliphatic and aromatic (neutral) carbons was observed at 285.0 eV. The C_{1s} peak observed at around 286.7 eV can be assigned to ethereal carbon of PVA and carbons adjacent to nitrogen atoms in the amphiphile. Also, the C_{1s} peak corresponding to the carbonyl carbon was observed at around 288.8 eV. The C_{1s} peaks belonging to fluorocarbon are observed at a higher binding energy region. The peaks at 292.0 and 294.5 eV were assigned to the CF_2 and CF_3 groups, respectively. The C_{1s} peak observed at 286.7 eV is mainly due to PVA. On the other hand, the C_{1s} peaks at 292.0 and 294.5 eV arise from the fluorocarbon groups of the amphiphile. the relative C_{1s} intensity from fluoro-

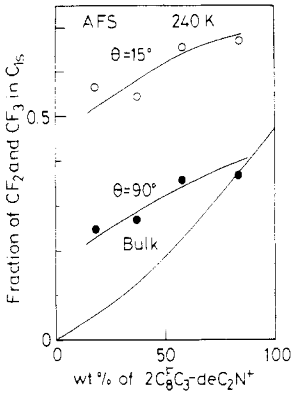

Figure 8. Variation of fraction of fluorocarbon in the total carbon atoms on AFS of the composite thin films with weight percent of fluorocarbon amphiphile at the takeoff angle of 15° and 90°. "Bulk" indicates the magnitude of fraction of fluorocarbon in total carbon atoms estimated from bulk composition.

carbon to the total C_{1s} intensity may indicate the fraction of fluorocarbon in the total carbon on the surface. The relative intensity of fluorocarbon in the total C_{1s} for a takeoff angle of 15° was larger than that for a takeoff angle of 90°. The sampling depth in the case of the takeoff angle of 15° is one-fourth in comparison with that for 90°. This indicates that the concentration of fluorocarbon on the outermost layer is larger than in the inner region.

Figure 8 shows the variation of the fraction of fluorocarbon in the total C_{1s} for AFS of the composite membrane with the weight fraction of fluorocarbon amphiphile. "Bulk" indicates the fraction of fluorocarbon in the total carbon calculated from the elemental composition of the each specimen. For a takeoff angle of 90°, the fraction of fluorocarbon on AFS increased with the bulk weight fraction of amphiphile. The fraction of fluorocarbon on AFS with the lower bulk weight fraction of amphiphile for the takeoff angle of 90° was much greater than that for the calculated bulk value. This indicates the enrichment of the fluorocarbon amphiphile on AFS due to the much lower surface free energy of the fluorocarbon group in the amphiphile. However, with an increase in the weight fraction of amphiphile, the fraction of fluorocarbon approaches the bulk value. The fraction of fluorocarbon for the takeoff angle of 15° is larger than that of fluorocarbon amphiphile itself (100 wt % fluorocarbon amphiphile). This indicates the orientation of the fluorocarbon group to the air and is in accord with the bulk aggregation state as confirmed by wide-angle X-ray diffraction measurement. Since the photoelectron mean free path in a Langmuir–Blodgett (built-up) film such as stearic acid and arachidic acid is 4–5 nm,[15] the sampling depth for a takeoff angle of 15° is estimated to be 3–4 nm. On the other hand, the sampling depth is estimated to be around 12–15 nm for a takeoff angle of 90°. Since the fluorocarbon membrane concentrated at AFS, it is reasonable that the fraction of fluorocarbon for the takeoff angle of 15° is larger than that for 90°. The surface coverage of the composite thin film with fluorocarbon amphiphile is due to the lower surface free energy of fluorocarbon groups compared with that of PVA. The interfacial free energy between air and the composite thin film is minimized when the outermost surface is covered with CF_3 groups. This is attained by orientation of fluoroalkyl chains to the surface of the composite thin films. Similar surface enrichment of the component with lower surface free energy has been observed for some block copolymer consisting of hydrophilic and hydrophobic groups.[16-20] Since the number ratio of fluorine to carbon atoms is proportional to the fraction of fluorocarbon in C_{1s}, a similar trend was observed for the variation of the number ratio of fluorine to carbon atoms on AFS of the composite thin film. As we have previously reported, permeation of oxygen through the composite thin films is faster by a factor of 2.4–2.7 than that of nitrogen.[11] This characteristic property was observed for the specimen containing a small amount of fluorocarbon amphiphile (19 wt %) in the composite thin film. This may be related to the surface coverage of the composite thin film with a fluorocarbon group. As the fluorocarbon group has a high affinity toward oxygen compared with nitrogen, the fluorocarbon group on the surface of the composite thin film increases the solubility of oxygen on the film surface.

Conclusion

The surface structure and state of aggregation of composite thin films consisting of poly(vinyl alcohol) and fluorocarbon amphiphile have been studied. The fluorocarbon amphiphile formed bimolecular lamellae in the composite thin film. Wide-angle X-ray diffraction study reveal that these bimolecular lamellae are oriented parallel to the surface of the composite thin film. It is apparent from X-ray photoelectron spectroscopy that even in the case of a small amount of fluorocarbon amphiphile, the amphiphile is enriched on the outer surface of the composite thin film due to the small surface free energy of fluorocarbon groups.

Registry No. PVA, 9002-89-5; $(F_3C(CF_2)_7CH_2CH_2CO_2CH_2CH_2)_2NCOCH_2N^+(CH_3)_3Cl^-$, 91362-66-2.

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