

Surface Modification of Ethylene-Tetrafluoroethylene Copolymer Film by Direct Fluorination in Liquid Media

(¹Grad. Sch. of Eng., The Univ. of Tokyo, ²AGC Inc.) ○Eisuke Yasuo,¹ Masafumi Sugiyama,¹ Yuichiro Ishibashi,² Satoru Hommura,² Takashi Okazoe,² Daisuke Kawaguchi¹

Keywords: Fluorine; Fluoropolymer; Ethylene-tetrafluoroethylene copolymer; Direct fluorination

Surface modification has been applied to polymer films used in applications such as coatings, electronic devices, and biomaterials. One of the promising surface modification technologies is direct fluorination, where molecular fluorine reacts with generally stable C–H bonds to give C–F bonds. The advantage of this method is that it imparts properties such as chemical resistance and water/oil repellency.^{1,2} Although a desired condition for this purpose is that it does not disrupt the higher-order structures of the polymers, the aggregation structures of the polymers after the fluorination have not been clarified yet. The objective of this study is to obtain a guideline for surface modification of polymer film by direct fluorination retaining the higher-order structures. To do so, we apply direct fluorination in a liquid media to a biaxially oriented semi-crystalline polymer film made from ethylene-tetrafluoroethylene copolymer (ETFE) under the condition as mild as possible.

A 25 μm thick ETFE film was immersed in CFE-419 (CClF₂CClF₂OCF₂CF₂Cl) and fluorinated by flowing 20% F₂/N₂ gas. As a result of the substitution of C–H for C–F, the mass of the film increased. The rate of mass increase could be regulated by controlling the reaction conditions, and it reached a maximum of 26%. The most fluorinated film (LF_ETFE25_26) remained transparent. Furthermore, the contact angles of H₂O and CH₂I₂ for LF_ETFE25_26 were larger than those for the pristine ETFE film (Fig. 1). These results indicated that the ETFE film at the surface was fluorinated without any significant damage and became more resistant to water and oil. In the presentation, we will discuss the effects of direct fluorination on higher-order structures and material properties of ETFE film in more detail.

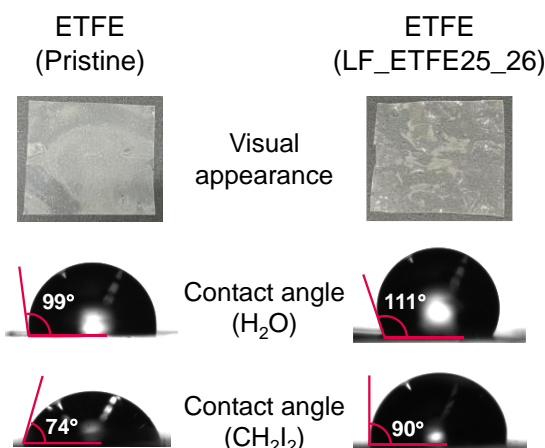


Fig. 1 Visual appearance and contact angle images of pristine ETFE and LF_ETFE25_26.

1) Bilnov, I. A. *et al. J. Fluorine Chem.* **2020**, 234, 109526.

2) Blinov, I. A. *et al. J. Fluorine Chem.* **2021**, 246, 109777.