

Title	エチレン - テトラフルオロエチレン交互共重合体の熱安定性と不安定流動に関する研究
Author(s)	小寺, 省吾
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Description	Supervisor:山口 政之, マテリアルサイエンス研究科, 博士

ABSTRACT

Fluoropolymers are categorized in one of the oldest high-performance materials, and the history dates back to discovery of polytetrafluoroethylene (PTFE) in 1938. Although their commercial market is smaller than typical commercial polyolefin resins such as polyethylene and polypropylene, fluoropolymers are becoming more and more important materials industrially because of their unique properties.

In this study, ethylene-tetrafluoroethylene copolymer (ETFE), an industrially important material, is focused to elucidate the basic properties and obtain the basic knowledge about melt processing through the analysis of rheological properties.

In Chapter 1, the historical background of the research on ETFE through the literature review and the problems left unfinished are mentioned.

In Chapter 2, the oscillatory shear modulus in the molten state is evaluated carefully considering the rheological change during the measurement at high temperature for ETFE. The results provide the information on the molecular weight distribution as well as the degradation behavior, which is affected by the environmental condition, i.e., the existence of oxygen. Even under a nitrogen atmosphere, ETFE is thermally unstable in the molten state; ETFE shows random chain scission reaction without crosslinking. The steady-state shear compliance J_e^0 , which depends on the molecular weight distribution greatly, is not changed during the chain scission. It suggests that the chain scission occurs with keeping the molecular weight distribution. Considering the classical theory on the random scission reaction, the experimental result indicates that M_w/M_n of the initial ETFE sample, prior to the exposure to thermal history, is closed to 2. In contrast, under air condition, ETFE shows crosslinking reaction even in a cone-and-plate rheometer. The degree of crosslinking is quantitatively estimated by the plateau modulus G'_{plateau} in the low frequency region. The result suggests that the crosslinking occurs as a first order reaction.

In Chapter 3, Flow instability of ETFE at the capillary extrusion is evaluated. It is found that ETFE shows several types of flow instabilities. In relatively low shear rate region, the shark-skin failure appears beyond the critical shear stress 7.9×10^4 Pa, which usually decides the maximum production speed at extrusion. Furthermore, the slip-stick failure occurs at 1.8×10^5 Pa and wavy melt fracture, originated from the flow instability at die entrance, appears over 3.5×10^5 Pa. It is interesting to note that quasi-stable flow region, so-called super-extrusion, is detected between slip-stick and wavy melt fracture regions. Since the surface of the extruded strand is smooth enough without volumetric distortion, ETFE can be processed at a high out-put rate condition by the steady slippage. The slip velocity is characterized by the Mooney method. The critical shear stress of the slippage on the wall is found to be 1.8×10^5 Pa, which corresponds to the onset stress of the slip-stick failure.

Key Word : rheology, ETFE, polydispersity, flow instabilities, critical shear stress