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Influence of the third monomer component on the temperature-dependent crystallite modulus and tie chain fraction evaluated for ethylene-tetrafluoroethylene copolymers

Atsushi Funaki [a,b], Kohji Tashiro [a,*]

[a] Department of Future Industry-Oriented Basic Science and Materials, Graduate School of Engineering, Toyota Technological Institute, Hisakata 2-12-1, Tempaku, Nagoya 468-8511, Japan
[b] Research and Development Division, Asahi Glass Co., Ltd., Yokohama, Kanagawa 221-8755, Japan

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ABSTRACT

Temperature dependence of apparent crystallite modulus along the chain axis E_c^{app} has been measured on the basis of X-ray diffraction measurement under the assumption of homogeneous tensile stress distribution for the uniaxially-oriented ethylene-tetrafluoroethylene (ETFE) alternating copolymers with and without the third monomer component of short or long side groups. The E_c^{app} of the 2-components alternating ETFE copolymer was found to decrease remarkably in the phase transition temperature region between the low- and high-temperature phases at around 80 °C. For the ETFE copolymer sample with the third comonomer component of long C_4F_9 side groups the E_c^{app} was found to show the similar temperature dependence to that of the pure alternating copolymer although the E_c^{app} value itself was slightly lower than the latter. The ETFE copolymer with short CF_3 side groups was found to show remarkably low E_c^{app} value in the temperature region from −50 to 50 °C since the crystal structure transferred already to the high-temperature disordered phase in this temperature region. The bulk Young's moduli of these copolymer samples, estimated by the dynamic viscoelastic measurements, were analyzed on the basis of a complex mechanical model consisting of parallel and series sequences of E_c^{true} and E_a, where E_c^{true} and E_a were the true moduli of the crystalline and amorphous regions, respectively. The temperature dependences of the bulk moduli observed for these three samples were successfully reproduced by estimating the E_c^{true} as a function of temperature. The E_c^{true} estimated at a low-temperature, was 215 GPa for ETFE 2-components sample, which was consistent with the value 230 GPa calculated theoretically for the planar-zigzag chain conformation. The parallel crystalline component, which was assumed to be a kind of taut tie chain to support the mechanical toughness of the bulk sample, was found to be lower in population for ETFE 2-components sample and higher for the copolymer samples containing the third monomer component. This tendency is consistent with that of the actually-observed stress crack resistance or the mechanical toughness in a high-temperature region near the melting point: ETFE < ETFE-CF3 < ETFE-C4F9. In this way, the terpolymer sample has an important role to create the higher content of taut tie chains, resulting in the higher stress crack resistance.

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1. Introduction

Ethylene (E) - tetrafluoroethylene (TFE) alternating copolymer (ETFE) is one of the melt-processable fluororesins. Because of the excellent thermal and chemical durability and electric property, ETFE is used for such various industrial applications as chemical equipment materials, wire coating insulations, *etc* [1]. These properties, in particular the mechanical and thermal properties are dependent on the content of E and TFE monomer units in the skeletal chain [2].

The alternating ETFE copolymer of 50 mol% TFE monomer content is semicrystalline polymer and the crystal structure was investigated extensively [3–7]. As reported in the previous paper [7], the low-temperature phase consists of the parallel array of almost fully-extended zigzag chains with some degree of relative height disorder along the chain axis. This low-temperature phase transforms to the high-temperature phase at around 100 °C, in which the zigzag chains experience the partial trans-gauche conformational exchange and these slightly disordered chains are

* Corresponding author. Tel.: +81 52 809 1790; fax: +81 52 809 1793.
E-mail addresses: ktashiro_001@yahoo.co.jp, ktashiro@toyota-ti.ac.jp (K. Tashiro).

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