

SHEAR AND ELONGATIONAL FLOW BEHAVIORS OF LONG CHAIN BRANCHED ETFE MELTS

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Abstract Rheological behavior of alternating ethylene-tetrafluoroethylene copolymer (ETFE) under shear and elongational flow was studied. Linear ETFE showed typical rheological behaviors as well as other linear polymer such as polyethylene and polypropylene. ETFE with long chain branch, however, showed outstanding behaviors. The branched ETFE indicated high G' at low frequencies, slow relaxation of relaxation modulus $G(t)$, weak strain dependency of damping function. Under elongational flow the branched ETFE showed strong deviation of elongational viscosity from linear viscoelastic regime. This suggests enhanced processability of ETFE in film casting, film blowing, foaming, blow molding.

Keywords: ETFE, fluoropolymer, rheology, dynamic viscoelasticity, elongational viscosity

Introduction

Ethylene-tetrafluoroethylene copolymer (ETFE) is widely used in many fields such as automobile, modern construction, airplane, solar battery panel areas due to the high chemical and thermal resistant, flame retardancy, weathering, an electric insulation properties. Therefore ETFE is intensively explored on the molecular parameters, microstructures, crystallization behaviors, flow behaviors under steady shear, flow instabilities. However, ETFE is one of typical linear polymers and the improvement of the rheological behavior by introducing the long chain branch has not been reported.

Now more advanced control of rheological behavior of ETFE is required for the wider applications and precise processings in which ETFE has not been utilized owing to the limited rheological properties so far. In this paper we try to introduce long chain branch into ETFE and the shear and elongational flow behaviors are reported.

Experimental

We used conventional ETFE (C88AX, Asahi Glass Co., LTD, Japan) and ETFE copolymerized with divinyl compound, which is indicated as ETFE-B. ETFE-B of weight percentages of 5, 10 and 30 was blended with ETFE by twin-screw extruder, indicated by notations of ETFE5, 10, 30, respectively.

Dynamic strain, frequency and temperature sweep measurements were performed by Physica MCR-301 (Anton Paar). Dynamic frequency tests were conducted from 0.1 to 100 rad/s at constant strain less than 0.05 and temperatures of 270 °C using parallel fixture. Elongational viscosity was measured by rotational rheometer (Ares, TA instruments) at constant rates and temperature of 270 °C.

Mono-layer T-die cast film extrusion was carried out by twin-screw extruder ($\phi=15\text{mm}$, ULT-nano, Technovel Co., Japan). External gear pump was used for constant volumetric flow rate.

Results and Discussion

Fig.1 shows storage (G') and loss modulus (G'') of ETFE and ETFE-B at 270 °C. ETFE indicated terminal flow behavior at low frequency range. On the other hand, ETFE-B synthesized with divinyl compound showed much elastic viscoelastic behavior. Within the measured frequency G' was always higher than G'' . G' is parallel to G'' at high frequency and the slope of G' leveled off with decreasing with frequency. This means an existence of very long time relaxation component.

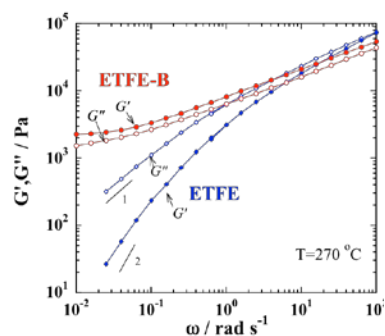


Fig.1 Storage and loss modulus of ETFE and ETFE-B at 270 °C

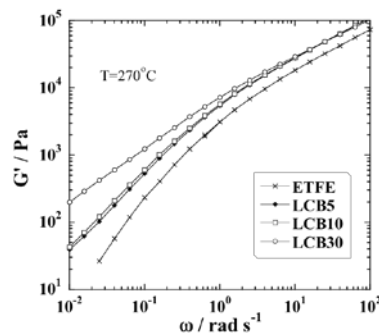


Fig.2 Storage and loss modulus of ETFE blended with ETFE-B (5, 10, 30 wt%) at 270 °C

Fig.2 shows linear viscoelasticity of ETFE blended with ETFE-B (5~30 wt%) at 270 °C. At high frequency G' 's of the blend samples were slightly higher than ETFE. G' of the blends at low frequency increased with increasing the weight ratio of ETFE-B. This is due to introduction of long relaxation time component of ETFE-B which dispersed in ETFE.

Transient elongational viscosity of ETFE and ETFE-B blends are illustrated in Fig.3. Linear ETFE mere showed smooth increase of elongational viscosity. The curves were independent of strain rate and merged into one curve. The elongational viscosity of ETFE blended with EtFE-B exhibited steep increase at a certain time, depended on the strain rate. ETFE30 showed the strong increase of elongational viscosity in comparison with ETFE10. This strong strain hardening is nonlinear behavior and never expected to linear ETFE. A small amount of the divinyl compound was used to copolymerize with ETFE. The branch structure can be expected for copolymerization of ethylene, tetrafluoroethylene and divinyl compound. If the star-type branching structure was formed for ETFE-B, the nonlinear viscoelastic behavior should not changed the way graft, pom-pom and random types branched polymer do under elongational flow, while the linear viscoelastic response was changed. Therefore we

consider that ETFE-B includes long chain branched molecules with two branching point at least.

We carried out T-die film casting extrusion of ETFE and ETFE-B blends. It was found that the neck-in length was reduced according to the incorporated ratio of ETFE-B, comparing with that of linear ETFE. In the film casting uniaxial flow is dominant at edge part of the film, while the rest is mainly subjected by planar flow. We consider that the strain hardening behavior of ETFE-B suppressed the neck-in length of casted film.

Conclusions

ETFE was modified by the incorporation of divinyl compound in the copolymerization process. ETFE-B copolymerized with divinyl compound and the blends with ETFE showed very long relaxation time and pronounced strain hardening behavior under elongational flow which can never be expected for conventional fluorinated polymer. We confirmed that the enhanced rheological behavior provide the beneficial effect on the T-die film casting extrusion process.

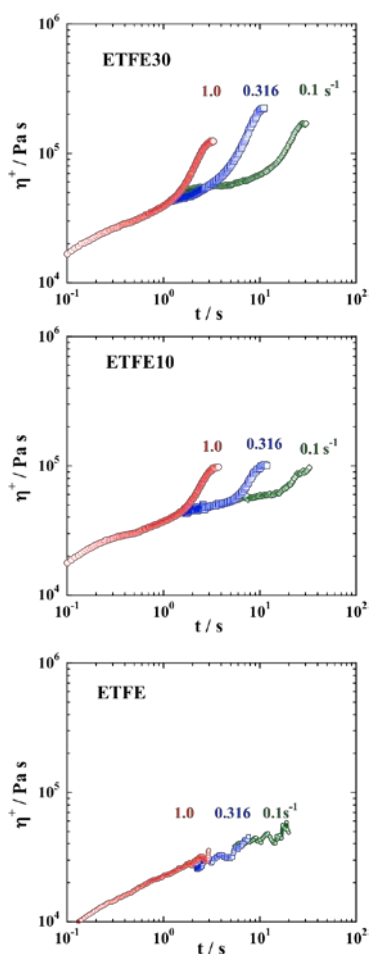


Fig.3 Transient elongational viscosity of ETFE, ETFE10, ETFE30 at 270 °C