Rheological characterization of polyethylene terephthalate resins using a multimode Phan-Tien-Tanner constitutive relation

Abstract  Linear viscoelastic, shear, and extensional rheological characterization of linear and branched Poly(Ethylene Terephthalate) resins (PET) was carried out by means of both a parallel-plate and capillary rheometers. Before loading into the rheometers, the polymer pellets were thoroughly dried at well-characterized conditions long enough to obtain consistent and reproducible results. Continuing polymer degradation and poly-condensation reactions in the relatively open environment of the parallel-plate rheometer were accounted for by correcting the data using material-time superposition. The rheological data obtained were used to fit by nonlinear optimization, the linear relaxation spectrum and nonlinear parameters of a multi-mode Phan-Thien and Tanner (PTT) constitutive relation. It was found that this model can represent rheological data for PET resins very well and as a result may be used in relevant processing flow simulations, i.e. film casting.

Key words  Polyethylene terephthalate – Phan-Thien Tanner model – material time correction – mutating materials

Introduction

Two of the main applications of polyethylene-terephthalate (PET) resins are film casting and extrusion coating of sheet material. Efforts to increase production speed or reduce film thickness by going to higher draw ratio (take-up roll speed/die exit melt speed) are limited by edge neck-in and bead formation, but mainly by process instabilities that give rise to spontaneous thickness and width oscillations (draw resonance, edge wave) (Pakula and Fischer, 1981).

Computational fluid mechanics modeling can help predict such instabilities and extend the parameter range of stable and defect-free operation (so-called “process operability window”). A predictive model requires a constitutive relation that adequately describes the rheological response of the melt at the shear and extension rates of the process. Such a relation is usually determined by testing the material in simple rheometric flows such as small-amplitude oscillatory shear flow between parallel plates and finite-rate flow through capillaries. Serious difficulties are encountered in rheological testing of condensation polymers like PET, however: 1) the rheological properties are greatly affected by moisture (White and Yamane, 1985; Jabarin and Lofgren, 1986); therefore, the material must be carefully dried before testing. 2) The open environment (nitrogen, vacuum, or dry-air) of the parallel-plate rheometer facilitates rapid withdrawal of reaction byproducts and shifts poly-condensation and/or degradation reactions to high conversions (Dealy and Wissbrun, 1990). Therefore, a procedure is needed to reduce the data to zero-time, i.e. the moment of loading before any structural changes took place.

In this paper linear viscoelastic, shear, and extensional rheological characterization of three industrial PET resins were carried out at drying conditions that were iteratively determined to obtain consistent and reproducible data. The data were then used to fit by non-
linear optimization, the linear relaxation spectrum and additional nonlinear parameters of a multi-mode constitutive relation proposed by Phan-Thien and Tanner (Phan-Thien and Tanner, 1977). The fitted relation will be used in the future in a finite-element model of the isothermal film casting process in the casting span in order to detect the operability window of the process as a function of the molecular structure of the PET resin used.

Materials

Three Polyethylene Terephthalate (PET) resins of different molecular weight and structure were studied. One of the resins had a linear structure, commercially known as Hoechst Celanese T-89 (a bottle resin). Here, it is denoted as PET-1. From the other two, PET-2 also has a linear structure although a smaller molecular weight (deduced from viscosity comparison) compared to PET-1; finally, PET-3 is a branched polymer. PET-1 and PET-3 have a melting point in the range of 240–250 °C determined from Differential Scanning Calorimeter analysis (DSC) while PET-2 has a higher one falling in the range from 255–265 °C.

Based on the DSC results, the rheological measurements were safely conducted in the range of 260–300 °C for PET-1 and PET-3, and 270–300 °C for PET-2. Above 300 °C, the polymers degrade relatively fast and it was impossible to get reliable measurements.

Rheological measurements

Two types of rheological measurements were carried out: i) linear viscoelastic measurements (mainly frequency sweep experiments from 0.1–500 rad/s) on a Rheometric Scientific SR-200 (stress-controlled rheometer). We used the parallel plate geometry using disposable plates with diameters 25 mm and 40 mm. The linear measurements were used to fit the viscoelastic spectra with a small number (typically 3–4) of modes. They were also used to study the time-dependent structural changes of the resins and to reduce the data to zero time by applying material-time superposition; ii) a capillary rheometer operated at constant rate was used by means of which the shear and extensional viscosities at high rates were determined. The latter were determined using the Cogswell’s analysis (Cogswell, 1972). The dynamic viscosity data were compared with the shear ones in order to check the applicability of the Cox-Merz rule (Dealy and Wissbrun, 1990).

Among various drying procedures tested, two gave consistent and reproducible results: vacuum drying at 160 °C for at least 6–10 h or vacuum drying at 130 °C for 18–24 h. It was also found that compression molding of the polymer disk samples for the parallel-plate viscometric measurements resulted in irreversible structural changes of the material that were manifested as inconsistent rheological data regardless of drying procedure. For all results presented below, the polymers were always loaded into the rheometers in the form of dried pellets. Care was taken to avoid any formation of bubbles during loading.

Figure 1 illustrates the effect of drying on the rheological properties of PET-1 at 260 °C. Closed symbols refer to dried pellets and open to not dried. Not drying decreases the properties by almost one order of magnitude.

Fig. 1 The effect of drying (160 °C for 7 h) on the rheological properties of PET-1 at 260 °C. Closed symbols refer to dried pellets and open to not dried. Not drying decreases the properties by almost one order of magnitude.