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Addition of filled or unfilled fluoropolymers and their effects on the electrification of a metallocene polyethylene during capillary flow

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Abstract

During the extrusion of polymers, the extrudates exhibit distortions at high shear rates such as sharkskin, spurt or gross melt fracture that limit industrial production rates. One solution to reduce or eliminate these defects is to induce slip at the die wall or in the polymer bulk for example by adding some polymer processing additives (PPA).

In this study, we used the addition of different fluoropolymers with and without inorganic fillers to promote wall and interlayer slippage in a metallocene polyethylene (mPE). As expected, defects onset was delayed and shear stress was decreased in any case due to the increase of slip velocity.

In a previous work, we showed that the electrical charging of the extrudate during the extrusion could be correlated with slip velocity. Present results confirmed the relationship between electrical charging and wall or interlayer slippage. Indeed, the higher the amount of PPA without filler in the melt, the higher the wall-slippage and the higher the electrification. The filled fluoropolymer exhibited a more efficient postponing of extrusion defects than unfilled ones concomitant with a strong increase of the extrudate electrical charging. Finally, electrical charging versus wall-slippage curves witnessed the influence of additives concentration and nature on electrification as expected from the double-layer theory.

Keywords: Fluoropolymer; Metallocene polyethylene; Electrical charging; Flow instabilities; Electrical double layer; Wall-slippage

1. Introduction

Since the late 1950s, extrusion instabilities have been widely studied due to their economical and theoretical interest [1]. Elimination of the instabilities that limit the processibility of polymers is possible and many ways were proposed to obtain it.

On one hand, many studies examined the question of slip and its influence on the observed extrusion instabilities [2–4]. Indeed, the role of slip is dominant in the occurrence and in the postponing of extrusion distortions. In this article, we will consider two types of slip.

The first one corresponds to the wall-slippage, i.e. to the violation of the no-slip boundary condition at the die wall. It is well-known that promoting wall-slip conditions is an effective method to eliminate some flow instabilities during polymer extrusion [5,6]. Different ways are possible to induce wall-slippage, for example by coating the die wall with slippery layers, such as Teflon™ [5,7], or by choosing high-surface energy alloys as die materials [2,8]. However, among all these techniques inducing wall-slippage, the most widely used industrial method is to add polymer processing aids (PPA) in the mainstream polymer [9,10]. In the case of fluoropolymer PPA, the mechanism of wall-slip generation has been elucidated: since the fluoropolymer droplets are immiscible in the melt, they migrate to the outside of the melt flow during the extrusion and form a coating layer on the metal die. Then, the polymer slips at the PPA/polymer interface [11,12].

A second type of slip can be considered in some particular cases of polymer extrusion with various additives. Indeed, the addition of mineral fillers such as calcium carbonate generally increases the viscosity of the melt [13]. However, when the mineral particles are coated by a lubricant layer (such as fatty acid for $CaCo_3$) a decrease of the viscosity can appear that is generally attributed to an internal lubrication, i.e. a slip in the bulk of the melt [14]. The resulting viscosity reduction by additives is often termed the "Toms effect" [15].

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Recently, Liu et al. [16] showed that the use of inorganic fillers/polyethylene glycol (PEG) binary processing aid (BPA) have better effect on viscosity reduction of metallocene linear low density polyethylene (mLLDPE) than PEG alone. To explain this improvement, they assumed that an encapsulation structure with a core of inorganic filler and a shell of PEG lubricant is formed during the preparation of the BPA. This structure promotes the interlayer slippage of the mLLDPE melt on the PEG layer coating the inorganic particles. Note that in the same time, PEG coating of the die wall is also present. Finally, the global viscosity reduction can be attributed to the both interlayer and wall-slippages.

On the other hand, the first study on polymer melt electrification was performed by Vinogradov et al. [17] and later by Dreval et al. [18,19]. These authors established a link between slip velocity and flow electrification of polymer melt during spurt instability. They referred to the triboelectrification theory to explain the electrification phenomenon, but they did not propose any clear mechanism for this electrification. From the same hypothesis of tribogeneration of the electric charges, Ohara [20] proposed a mechanism of charge transfer between the metallic die and the polymer segments anchored on it. The variation of the triboelectrification was thus linked to the molecular polymer chains dynamics. More recently, Perez-Gonzalez et al. worked on polyethylene also during spurt defect [21,22]. They measured electrification only when strong slip was observed, and assumed that the charge build-up was produced by dynamic friction. However, no precise mechanism or quantitative model was proposed to justify the link between slip and electrification of the extrudate. All these authors measured electrical charges only during the unstable regime or during stable regime when strong slip was observed by using a brass die [8].

Another mechanism of extrudate electrification has been proposed by Taylor et al. [23,24]. Contrary to the above studies, flow electrification measurements were carried out under stable regime although no slip was detected. These authors invoked the double layer theory, extrapolated to the polymer case, to explain the electrification phenomenon (see Section 2.1). Finally, they proposed an analytical model to explain their electrification curves.

In a first paper [25], we showed that similar to Taylor's studies it was possible to measure electrification of the extrudate even under stable regime and no slip conditions. However, these types of measurement were possible only thanks to the high resolution of our electrical measurement set-up. For example, in the particular case of the pure metallocene polyethylene (mPE), we measured weak electrical charges in the range of 10^{-2} to 10^{-1} mC m^{-3}. These values are significantly lower than the ones around 10 mC m^{-3} which are generally observed during spurt defect or under strong slip [17,18,26]. However, we also noticed the strong influence of the slip on the electrification, and we proposed to use the electrification measurement as a simple way to evidence slip phenomenon.

In the present work, in order to better elucidate the relationship between slip and electrification, we studied the influence of different PPA (with or without fillers) on the slip and on the electrification of the same mPE. We were not interested in improving the postponing of the extrusion defects or in explaining the mechanism of PPA action, but in using the PPA as promoters of the slip. More precisely, we tried to evaluate the respective influence of (i) wall sliding in the case of PPA without fillers and (ii) interlayer slippage for filled PPA.

It is well-known that the set-up of the fluoropolymer coat is not instantaneous [12]. Thus to determine at any moment the die surface state, we first studied the kinetic of the fluoropolymer layer development. This allowed us to know when the steady state was reached, i.e. when electrification measurements could be correctly performed. Then, for each PPA we performed rheological and electrical measurements when steady state was established at different loads of PPA. A tentative correlation is proposed between electrification and the evaluated slip velocity. To analyse our experimental results, we used the double layer theory that has been proven to be a good way to describe polymer electrification phenomenon [24,25].

2. Pre-required

2.1. Double layer theory: recall of main results

Electrokinetic phenomena were widely studied and authors have developed a double layer theory to explain charge generation phenomenon. This theory was fully described elsewhere [27,28], and only main results are recalled here. This theory was first mentioned for Newtonian hydrocarbons liquids flow through a metallic capillary. Inside liquids, charged species are always present such as ionic impurities. In the case of polymer liquids some parts of polymer chains could also be charged. When these charged species are put in contact with a metallic surface, a preferential adsorption occurs for one type of ions (positive or negative) [29]. Charges accumulate on the metal surface and lead to the formation of an electrical double layer close to the capillary wall (Fig. 1). The first layer is an inner layer due to ions adsorbed at the wall of one or two molecular diameters thick. The second layer is a diffuse layer that balances the charge held on the capillary wall. An evaluation of its thickness

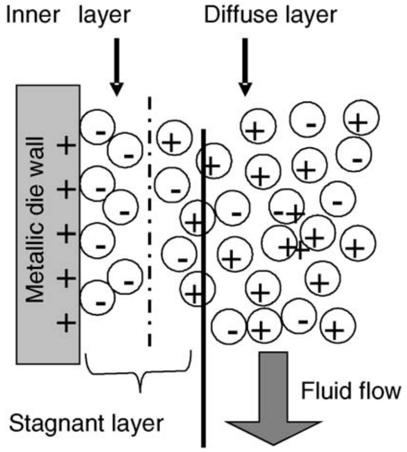

Fig. 1. Schematic diagram of an electrical double layer. The measured current at the die outlet corresponds to the excess charges convected by the fluid flow.