Elongational Flow

Elongational flow is a particular kind of flow involved in many industrially relevant processing operations of thermoplastics (such as fiber spinning, film blowing, foaming and thermoforming) in which the velocity gradient develops in the same direction as the flow itself.

1. Introduction

A large number of processing operations for polymeric materials having high industrial relevance are dominated by elongational flow, i.e., a stretching deformation that, depending on the specific process, can be uniaxial or biaxial [1][2]. Fiber spinning, film blowing, blow molding and foaming, among a few others, are typical examples of processing techniques, in which the polymer melt is subjected to elongational flow [3][4]. Actually, elongational deformation also occurs in some processes essentially dominated by shear flow, such as extrusion and injection molding [5]; the variation of the flow channels and the entrance in the die section in extrusion, or the injection of the melt into the mold gate, represent some examples in which the melt is subjected to components of elongation flow [6]. Besides, during the past few decades, plasticizing conveying methods and related devices (such as vane, eccentric rotors extruders and extensional flow mixers) based on elongational flow have been continuously developed, demonstrating shorter processing times and higher mixing effectiveness as compared to conventional shear-flow-dominated techniques [7][8].

The great relevance of these processing operations justifies the interest in the study of the rheological behavior of polymer melts when subjected to elongational flow, documented by a massive number of scientific papers in the last 50 years. In fact, a thorough knowledge of the processing behavior of polymeric materials when subjected to the elongational flow is of fundamental importance for predicting the melt behavior and obtaining straightforward criteria that allow for the selection of the proper material, as well as the optimization of the processing conditions [9][10].

Additionally, a characteristic feature of the elongational flow is its potential ability to modify the morphology of homogeneous polymer systems, through the occurrence of orientation phenomena of the macromolecular chains along the flow direction [11]. As a result, significant variations of the polymer microstructure and, thus, of its mechanical, optical or barrier properties can be obtained [12][13]. Interestingly, the ability of the elongational flow in inducing morphological changes has been documented also for polymer-based materials showing a multiphase microstructure, such as polymer blends [14][15] and micro- and nano-composites [16][17]. In particular, the application of the elongational flow during the processing of polymer blends causes a deformation of the droplets of the dispersed phase, leading to a modification of the blend morphology with a remarkable influence on the material final properties [18][19]. Similarly, it has been documented the effectiveness of the extensional flow in ameliorating the state of dispersion of micro- and nano-fillers in polymer-based composites. Besides, especially for composite systems containing anisotropic fillers, the application of the elongational flow during processing brings about some preferential orientation of the embedded particles along the flow direction [20][21], with beneficial effects on the overall performances of the material.

2. Rheological Properties in Elongational Flow

The rheological behavior in isothermal elongational flow has been widely studied especially for polymeric materials with a great industrial relevance, such as polyethylene (both high- and low-density), polypropylene and, in the recent years, polylactic acid and other biopolymers that attempt replacing traditional fossil fuel-based thermoplastics in many industrial applications. From a general point of view, it is well established that the content of long-chain branching has a remarkable effect on the elongational behavior of the polymer melt, leading to the occurrence of a strain-hardening behavior [22][23]. An interesting study by Wolff et al. [24] on the elongational properties of a commercial low-density polyethylene (LDPE)

demonstrated that, in the linear regime of deformation, the Trouton law was fulfilled, while, in the nonlinear regime, the presence of a large amount of long-chain branching induced the occurrence of strain hardening, with a rapid increase of the elongational viscosity as a function of the applied stress.

Most of the studies reported in the literature on the evaluation of the polymer rheological properties in elongational flow have been carried out in isothermal conditions, while less attention has been devoted to the rheological behavior of polymer melts experiencing non-isothermal elongational flow, notwithstanding its technological relevance for the assessment of the processing behavior of polymer melts. Similar to what was observed for isothermal elongational flow, polyethylene- and polypropylene-based systems are the most investigated materials, given the widely exploitation of these polyolefins in processing operations, in which the non-isothermal elongational flow is prominent [25][26]. As far as polyethylene-based materials are concerned, typically LDPE shows high values of melt strength and low deformability, while HDPE exhibits an opposite behavior [27]; the differences between the two materials can be ascribed to their dissimilar macromolecular architecture, pointing out the remarkable effect of the molecular weight and of the content of long-chain branching on the polymer rheological response.

3. Effect of Elongational Flow in Modifying Morphology and Mechanical Properties of Homogeneous Polymers

A fundamental characteristic of the elongational flow is related to its ability to induce a preferential orientation of the polymer macromolecules along the flow direction, thus affecting the material morphology. Furthermore, for semicrystalline polymers, the application of the elongational flow influences the crystallization kinetics and the morphology and orientation of the formed crystalline structures [28][29]. In fact, the alignment of the polymer chains along the flow direction reduces the energy barrier for the crystallization, as the state of the polymer chains is closer to that of the final crystal when they are in oriented configuration rather than arranged in random coils [30].

All these structural evolutions induced by the application of the elongational flow have, in turn, a remarkable influence on the material final properties and, especially, on its mechanical performances [31]. In particular, a very different behavior for semicrystalline and amorphous polymers has been reported. Briefly, for semicrystalline polymers, the application of an elongational flow usually results in an increase of the stiffness and a drastic decrease of the ductility as a function of the applied stretching [32][33]. In fact, it was demonstrated that the stable orientation of the macromolecular chains along the stretching direction achieved when these systems are subjected to elongational flow (especially in non-isothermal conditions) causes a progressive strengthening and stiffening of the material as a function of the draw ratio [34].

Otherwise, for amorphous polymers, the elongation at break typically increases upon extension, and a kind of brittle-to-ductile transition is observed. In this context, La Mantia et al. [35] studied the variation of the elongation at break for polystyrene filaments subjected to a spinning-like experiment as a function of the birefringence (which is indicative of the macromolecular orientation). The obtained results showed that the elongation at break abruptly increases at a specific birefringence value of $-6*10^{-3}$, after which a regular decrease is observed. Lastly, the elongation at break further increases at higher orientation values. This peculiar behavior, involving the occurrence of a sort of brittle-to-ductile transition, was ascribed to microstructural changes that occurred upon the application of the elongational flow; in particular, it was inferred that the more ordered morphology, involving oriented and stretched macromolecular chains, facilitates the macromolecular motion and improves the chain slippage. Furthermore, the compact arrangement of the parallel oriented and aligned polymer chains suppresses the formation and growth of cracks, bringing about to a ductile fracture [36].

Therefore, the knowledge of the structure-process-properties relationships in processing operations involving the elongational flow is fundamental for predicting the physical and mechanical properties of the final product, as well as for tailoring the processing conditions and/or the polymer properties according to the envisaged performances.

4. Morphology Evolution of Polymer-Based Blends under Elongational Flow

During the past years, the continuous demand for innovative materials caused a steadily increasing interest towards the production of polymer-based blends, thanks to the possibility to achieve functional materials with tailored properties using polymer commodities. However, most polymers are thermodynamically immiscible in the molten state, due to unfavorable interactions between the components and the small gain in entropy, resulting from the mixing of high-molecular-weight species [37]. As a consequence, polymer blends usually exhibit a heterogeneous morphology, which is characterized by the size and shape of the domains constituting the dispersed phase, as well as by their distribution in the matrix. Most commercial blends exhibit a typical droplet-like morphology, consisting in droplets of the dispersed phase embedded in

the matrix, though fiber-like or lamellar structures can be also achieved [38]. Since the microstructure of a polymer blend has a predominant influence on the material final properties, the prediction and control of the blend morphology are of fundamental importance for its end-use applications.

The phase morphology of a polymer blend surely depends on the chemical nature of the components and on their ratio; additionally, due to the deformability of the minor phase embedded in the matrix, when processed in the melt, an in situ morphology can be developed [39]. Therefore, the kind of flow that polymers underwent during the melt processing operation greatly affects the mechanism of deformation of the dispersed phase, thus remarkably influencing the evolution of the blend morphology and, consequently, the material final properties. It has been widely documented that the extensional flow is more effective than shear in deforming and breaking-up the droplets of the dispersed phase [40]. Besides, for immiscible blends containing high amounts of dispersed phase, the formation of elongated fibrils was frequently reported [41].

Figure 1 schematically depicts a possible mechanism explaining the droplet-to-fibril transition observed in immiscible blends subjected to elongational flow. During the application of the extensional flow, the macromolecules constituting the matrix phase, similarly to a homogeneous system, tend to orient and align along the flow direction; at the same time, the particles of the dispersed phase deform, giving rise to the formation of elongated structures, preferentially oriented in the stretching direction (**Figure 1**A). Once the critical capillary number is reached, the breakup of these elongated structures occurs, causing the formation of droplets of small dimensions that are further deformed by the action of the elongational flow, until the formation of microfibrils mainly oriented along the flow direction (**Figure 1**B).
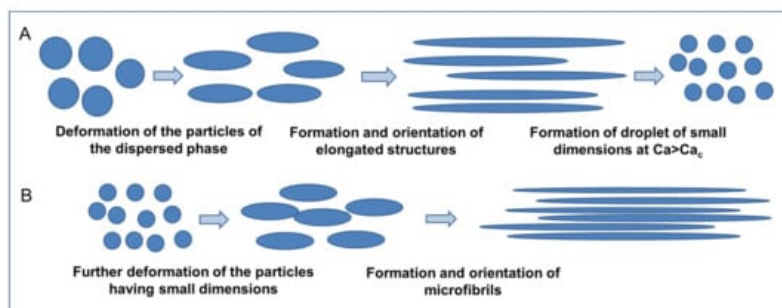
Figure 1. Schematic representation of the possible mechanism of the droplet-to-fibril transition in immiscible blends subjected to elongational flow: (**A**) Deformation of the original particles of the dispersed phase and (**B**) formation of microfibrillar structures.

Another fundamental factor influencing the development of the phase morphology during melt processing operation dominated by the elongational flow is coalescence; in fact, in the presence of intense interactions among the particles of dispersed phase, due to high concentration or restricted geometries, numerous collisions occur, hence possibly causing coalescence phenomena [42]. For instance, during melt spinning, the shrinking matrix compresses the droplets of dispersed phase, enabling them to migrate form the surface toward the center of the fiber and promoting coalescence events [43].

5. Morphology Evolution of Polymer-Based Composites under Elongational Flow

Polymer micro- and nano-composites are an interesting class of materials for studying the effect of the elongational flow in promoting microstructural variations, as the state of dispersion, the size and, possibly, the orientation of the embedded nanoparticles can evolve upon the application of uniaxial or biaxial stretching.

Some studies on composite materials containing graphite [44], halloysite nanotubes [45], hydrotalcites [46] or carbon nanotubes [47][48] documented a beneficial effect of the application of elongational flow on the final morphology and properties of the materials. More specifically, upon uniaxial or biaxial elongation, a partial destruction of the filler agglomerates usually observed in composites obtained through melt mixing occurs; besides, a preferential alignment of anisotropic filler and/or of particle clusters along the flow direction has been reported. Furthermore, it has been shown that all these morphological changes directly affect the final performances of the resulting materials; in general, superior stiffness, strength and optical and barrier properties are obtained for composite systems subjected to elongational flow, as compared to the isotropic counterparts.

The most striking results in terms of elongation-induced morphology evolutions have been obtained for polymer nanocomposites containing layered silicates [49][50][51]. Several studies documented a progressive orientation of the embedded clays as a function of the applied stretching, hence showing the already described typical behavior of other polymer-based nanocomposites. In addition, it has been shown that the presence of small amounts of dispersed clays can facilitate the alignment of the matrix macromolecules, as the presence of well-dispersed platelets suppresses the relaxation of the polymer chains, thus promoting a high orientation degree [52]. Furthermore, for nanoclay-polymer systems, two different phenomena can occur upon elongational flow, i.e. flocculation and re-aggregation of dispersed clays [53] or improvement of intercalation/exfoliation [54]. Therefore, the final morphology achieved in these materials upon extension depends on the prevailing mechanism. It has been demonstrated that flocculation events are favoured when the elongational flow is applied in the molten state to nanocomposites already showing an exfoliated morphology [54]. Furthermore, the polymer/clay interaction degree plays a fundamental role, as the achievement of a good adhesion between the two phases promotes the development of a "face-to-edge" morphology, causing clay re-arrangements and flocculation [55]. Finally, it has been documented that the amount of clay is a critical parameter in determining the prevailing mechanism, since an improved exfoliation upon extension was achieved for nanocomposites embedding low particle loadings; on the contrary, filler aggregation phenomena are favored in the presence of high clay loadings, as this condition magnifies the electrostatic interactions among the particles [56].

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