Effects of shear during the cooling on the rheology and morphology of immiscible polymer blends

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Abstract. The aim of this work was the generation of a microfibrillar structure in immiscible polymer blends using a new technique. The blend polymer model is the emulsion formed by a mixture of polypropylene (PP) with polystyrene (PS) in the proportion of PP10/PS90. In the first case the pellets of polystyrene and polypropylene were blended on the twin-screw mini extruder in the classical manner with different shear rates. In the second case, the same blend was prepared in the same way followed by a dynamic cooling at different shear rates. The phase morphologies of PP in the blend were determined by Scanning Electron Microscopy on two directions (transversal and longitudinal direction to the flow). In the two cases, the dispersed phase size decreased with the increase of the shear rate in the extruder. An anomaly was registered in the classical method at 200 rpm, where the size of the dispersed phase increases with the increase of the shear rate. The dynamic cooling technique recorded smaller diameters (4 to 5 times) of the dispersed phase compared to the conventional technique. In addition, the reappearance of the microfilaments at 200 rpm was observed. The rheological properties were determined by RS100 (Thermo Scientific Haake). Using this new technique, it was noticed that the elastic modulus increases with one decade compared to the classical method and the complex viscosity decreases with the increase of the shear rate. An anomaly was registered in the classical technique, where the dynamic viscosity at 200 rpm increases with increasing the shear rate in the extruder.

1. Introduction
Blending of polymers is an effective way to obtain new materials with improved properties [1]. Since most of the polymers are immiscible, thus a decrease of specific properties is usually observed. The extrusion of an immiscible polymer blend in which the dispersed phase forms in situ reinforced nodules or fibers is the preferable way to achieve the highest mechanical properties [2]. In order to obtain such structure, so called microfibrillar composites were developed [3-5].

The morphology of the dispersed phase is the key parameter which governs the all properties of the materials. It is directly related to the processing conditions and concentration of the dispersed phase [6]. Various phenomena were related to the dynamics of droplet such as deformation, rupture, time-
dependent behavior and coalescence. Several studies have been carried out in order to control the morphology of the blend polymer, such as the rapid cooling of the extruded in iced water technique [7] and quenching the extrudate [8-10]. The major studies were conducted on specific devices [11, 12]. Most properties of immiscible polymer blends depend essentially on the morphology development during the phase preparation [13]. The principal goal to structuring the polymer blends was to attain a possible finest morphology and good distribution of the dispersed phase in the matrix.

During the preparation of the blend polymer, a great diversity of morphologies (droplets, filament and co-continuous phases) can be obtained [1]. The final size and shape of the dispersed phase are determined by the competition between coalescence and breakup. Coalescence is a process in which two or more particles collide and physically merge into one particle. Two classes of coalescence play critical roles in the development of morphology during the processing of immiscible polymer blends [14, 15]. In the first class, the coalescence is caused by the thermal Brownian motion and, in the second class: the collisions are caused by hydrodynamic forces [16]. On the other hand the breakup of the dispersed phase during the extrusion of the polymer blends is mainly controlled by the interfacial tension, rheological properties and complex strain field of the extruder [17]. However, deformation and rupture of the droplets are governed by two factors: the viscosity ratio between dispersed phase and the matrix phase, and the capillary number which presents the ratio between the viscous and interfacial forces [18].

This investigation was performed on the extruder in order to approximate real conditions for the preparation of the polymer blend. The main goal of this study was to introduce a new technique for the preparation of the polymer blend. The classical technique consists in the blending at different shear rate followed by the solidification of the molten blend under air flow. However in this early stage, the static coalescence plays an important role. In order to suppress the static coalescence of the dispersed phase, the dynamic cooling technique was adopted to produce the finest system morphology and smallest droplet sizes. This technique was based on two parameters during the cooling stage (rotation speed and temperature). Due to the difference in sensitivity of the blend compounds, the temperature variation during extrusion can produce different ratios of viscosity in the blend and that gives an opportunity for manipulation finest droplet and fibrillar behavior in blends. The dynamic solidification of the dispersed phase due to the crystallization was shown to be a good way to improve the stability of the fibrillar structures with respect to the shear out during extrusion.

2. Experimental part

2.1. Materials
The materials used in this study were commercial grades. Standard polystyrene was supplied by BASF S.A (Germany). Its average molar mass was $M_w = 215160$ g/mol with polydispersity coefficient $I = 2.35$. Isotactic polypropylene (100-GA01) was produced by INEOS Company (Switzerland), with a melt flow index (MFI) of 0.9 g/10 min and density of 0.923 g/cm$^3$.

2.2. Sample preparation
The principal factor to take into account was the difference in temperatures between the dispersed phase (melting temperature) and the matrix phase (glass transition temperature). All polymers were dried at least 18 h in a vacuum oven at 80°C. The polymer granulate was pre-mixed and injected in the twin screw mini extruder (Thermo Haake) at 200°C. In the conventional technique the samples were extruded at (30, 60, 90, 120, 150 and 200) rpm and 200°C, followed by cooling stage on air in the extruder. The dynamic cooling technique used for structuring the blend polymers is described as follows. The sample was blended for 3 min at 200°C and 60 rpm, followed by a rapid change of the extrusion speed while keeping the same temperature. After 3 min, the cooling phase was started, maintaining the speed extrusion to the point of crystallization of the dispersed phase (maximum torque of the extruder), in order to freeze the generated microstructures (suppress of the static coalescence).
2.3. Scanning Electron Microscopy

A Hitachi S-3340 Scanning Electron Microscopy (SEM), operating at 15KV accelerating voltage, was used to observe the blend morphology. The surfaces taken from cryofractured samples were observed by SEM in two directions to the flow. After drying procedure, the samples were coated with gold-palladium thick film. The adopted technique to detect the morphological evolution was based on an image of the sample on two-dimensional (2D) object, because the fibrillar morphology can be viewed as droplets when the fibrils are observed perpendicularly to the flow direction. For this reason, it was suggested [19, 20] to examine the collection of images from two orthogonal planes [21]. An average of 50 to 100 particles per sample was examined.

2.4. Thermal properties

The thermal properties were carried out by Differential Scanning Calorimetry using a Q100 DSC (TA Instruments, USA), with samples of about 5 mg in aluminum pans under nitrogen atmosphere. The temperature and heat flow calibrations were performed using Indium ($T_m=156.6^\circ$C) at a heating and cooling rate of 10°C/min. The matrix (PS) presents a glass transition temperature of about 96°C and a melting and crystallization temperatures of the dispersed phase (PP) as 165°C and 112°C respectively. These parameters are valuable information, which enables us to get a large difference between the crystallization of the dispersed phase and the glass transition of the matrix temperatures.

2.5. Rheological properties

The rheological characterization of the pure and blends polymers was carried out using a stress controlled rheometer (RS 100) from Thermo Haake Rheostress, using parallel plate geometry (diameter 20 mm and a gap of 1 mm). Samples with 20 mm and a thickness of 1 mm were compression molded from the test material using hydraulic press (Carven-USA) at 200°C. For all measurements, the stress amplitude was fixed at 10Pa to insure the viscoelastic linearity of the response. All materials functions were determined in the frequency range from 0.001 to 10s$^{-1}$.

3. Results and discussions

3.1. Morphological observation

3.1.1. Static cooling technique blends morphology

Figure 1 shows the micrographs of PP10/PS90 blends prepared with different shear rates using static cooling technique. The micrographs on the left side were obtained on the perpendicular facet to the flow, on the right side the micrographs were photographed on the longitudinal facet. The sample sheared at 30rpm presents deformed droplets with a shape factor slightly greater than 1. The sample sheared at 60rpm presents a mixture of filaments and droplets oriented in the flow direction. The blend polymer sheared at high speed presents a circular shape of the dispersed phase without orientation; this is probably due to a static cooling stage. The dispersed phase has the necessary time to relax before the crystallization. It was found that the major reduction of the particle size of the dispersed phase occurs at an initial stage of less than 1 or 2min, during blending [13]. However, an anomaly was recorded at 200rpm, where the size of the dispersed phase increases with the increase of the extrusion speed. These observations are in good agreement with those obtained by [22, 23]. It is may be due to the intensity of the extrusion which promotes dynamic calescence of the dispersed phase.
Figure 1. Micrographs of the blends PP/PS (90/10) prepared with static cooling technique: extruded at different speeds (30, 60, 90, 120, 150, and 200rpm). All blends were photographed in both directions (transversal and longitudinal to the flow).

3.1.2. Dynamic cooling technique blends morphology

The morphology development obtained by dynamic cooling technique is shown Figure 2. When the sample was not cooled by dynamic technique, the dispersed phase was presented in the transversal side by circular coarseness form. In the longitudinal side, a fibrillar form of the dispersed phase was developed with length that exceeds 100µm. When the dynamic cooling technique was applied, the size of the dispersed phase decreases sharply. Reducing the size of the dispersed phase is inversely proportional to the increase of the extrusion speed. Fibrillar microstructure reappeared again in the speed extrusion of 200rpm with a shape factor of 20; this may be due to the extrusion intensity.

The treatment of the micrographs (Image J software) of the blends prepared with the two techniques was realized in terms of the average diameter of the dispersed phase (Table 1). The average diameter of the dispersed phase was decreased with increasing the extrusion speed in the two cases.

Table 1. Average diameters of the dispersed phase prepared by static and dynamic cooling techniques

| Sample             | PP0.9/PS (10/90) |
|--------------------|------------------|
| Extrusion speed (rpm) | d (conventional technique) | d (dynamic technique) |
| 30, (60/30)         | 2.5              | 0.75          |
| 60, (60/60)         | 1.8              | /             |
| 90, (60/90)         | 1.5              | 0.35          |
| 120, (60/120)       | 1.2              | 0.31          |
| 150, (60/150)       | 1.1              | 0.27          |
| 200, (60/200)       | 1.15             | 0.20          |
The dynamic cooling technique develops diameters five times lower than in the classical technique. This may due to the suppression of the coalescence in the cooling stage.

3.2. Rheological properties

3.2.1. Static cooling technique

Frequency sweeps were performed at the same conditions (F=0.001 to 10 s\(^{-1}\) and 200°C). Figure 3-a and Figure 3-b present respectively loss modulus and complex viscosity in function of the shear frequency for the blends prepared with the static cooling technique. All values of storage modulus were situated in between of those of the components of the blends Figure 3-a. A less decrease was noticed when the extrusion speed increases. An enhanced elasticity at low frequency is obviously shown. The shoulder in G’ of the blend with droplet represents an additional relaxation due to the deformation of the dispersed phase [24]. Molten polymers show constant viscosity (Newtonian behavior) only in the low frequency region. At higher frequency, the viscosity generally decreases with the increase of the shear rate, indicating a pseudoplastic behavior. The rheological properties of the blends were predominant by the matrix phase. An anomaly was observed in the evolution of the complex viscosity of the blend prepared at 200rpm, where the complex viscosity increases with the increasing of the extrusion speed. This may be explained by the increase of the size morphology of the
dispersed phase at the same extrusion speed (Table 1) [22-23]. At low frequencies a negative deviation behavior of the complex viscosity was noticed, which probably originates in slip at the interface [25-26] due to poor or insufficient adhesion between the matrix and the dispersed phase.

![Figure 3](image3.png)

**Figure 3.** Evolution of the rheological properties of the blends prepared at different extrusion speeds by static cooling technique.

#### 3.2.2. Dynamic cooling technique

Figure (4-a) shows the evolution of storage modulus of PP10/PS90 blends prepared with dynamic cooling technique. All the storage moduli are situated in between the moduli of the components. The elasticity of the blends was predominant by the elasticity of the dispersed phase. At high frequencies the storage moduli of the blends were superposed on the moduli of both components. The anomaly shown in the first case (static cooling) was suppressed when the cooling dynamic technique is used. All values of complex viscosities Figure (4-b) were situated in between the components of the blends (PP and PS). Increasing the rotation speed in the extruder decreases slightly Newtonian viscosity. The rheological properties of the polymer blends are predominated by those of the disperse phase, thus increasing the elasticity and viscosity of the blends. At low frequencies, a pronounced deviation on the elastic modulus was observed. It presents the additional relaxation of the dispersed phase [27]. Obviously, these rheological parameters deviating from linear rheological model seems a useful approach to assessing the critical point of phase separation in polymer blend [28].

![Figure 4](image4.png)

**Figure 4.** Evolution of the rheological properties of the blends prepared by different extrusion speeds by dynamic cooling technique.
4. Conclusion
In this study the morphology evolution in polymer blend composed by polypropylene (10%) and polystyrene (90%) was evaluated by two techniques, static and dynamic cooling. The new technique was based on the crystallization of the dispersed phase during the extrusion. The size of the droplets generated by the dynamic cooling technique is 4 to 5 times less than that generated by the conventional technique. The new technique minimizes the coalescence of the dispersed phase during the blend solidification. At high shearing, the cooling dynamic technique generated microfibrillar morphology with a high shape factor (20). In the two techniques, the reduction in domain size by the increase of the shear rate in the molten blends originates from the breakup of the droplets caused by the coalescence suppression effect. The storage modulus developed by dynamic cooling technique was higher compared to the conventional technique by one decade. At static cooling technique the elastic moduli and the complex viscosity were predominant by the matrix phase, at dynamic cooling technique; the rheological properties of the blends were predominant by the dispersed phase. The storage modulus in low frequencies region developed by the new technique present a pronounced deviation; this corresponds to an increase in elasticity and longer relaxation time compared to the matrix. The main result in this study is the important role played by the coalescence in the determining of the morphology of the blends.

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